

# TRANSACTIONS

OF THE

## AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

(INCORPORATED)

Volume 140

### IRON AND STEEL DIVISION 1940

PAPERS AND DISCUSSIONS PRESENTED BEFORE THE DIVISION AT THE MEETINGS  
HELD AT NEW YORK, FEB. 13-16, 1939; CLEVELAND, APRIL 26-28, 1939;  
CHICAGO, OCT. 23-25, 1939; NEW YORK, FEB. 12-15, 1940.

NEW YORK, N. Y.  
PUBLISHED BY THE INSTITUTE  
AT THE OFFICE OF THE SECRETARY  
29 WEST 39TH STREET



## *Notice*

This volume is the thirteenth of a series containing papers and discussions presented before the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers since its organization in 1928; one volume each year, as follows:

1928, Iron and Steel Technology in 1928 (later listed as Volume 80 of the TRANSACTIONS); 1929 (vol. 84), 1930 (vol. 90), 1931 (vol. 95), 1932 (vol. 100), 1933, 1934, 1935, 1936, 1937, 1938, 1939 and 1940, TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Iron and Steel Division.

This volume contains papers and discussions presented at the meetings at New York, Feb. 13-16, 1939; Cleveland, April 26-28, 1939; Chicago, Oct. 23-25, 1939, and New York, Feb. 12-15, 1940.

Papers on iron and steel subjects published by the Institute prior to 1928 are to be found in many volumes of the TRANSACTIONS of the Institute; in Vols. 37 to 45, inclusive; 47, 50 and 51, 53, 56, 58, 62, 67 to 71, inclusive; 73 and 75. Vol. 67 was devoted exclusively to iron and steel.

Iron and steel papers published in the TRANSACTIONS before the year 1936 may be found by consulting the general indexes to Vols. 1 to 35 (1871-1904), Vols. 36 to 55 (1905-1916), Vols. 56 to 72 (1917-1925), and Vols. 73 to 117 (1926-1935).

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THE MAPLE PRESS COMPANY, YORK, PA.

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## FOREWORD

The present volume of TRANSACTIONS of the Iron and Steel Division contains 22 technical papers with complete discussion, in addition to the Howe Memorial Lecture by Dr. Charles H. Herty, Jr., and the Round Table on Experimental Methods in the Study of Steelmaking held in New York in February 1939. The field covered by this collection of papers is exceptionally well-rounded; undoubtedly there are data in this volume of interest to every member of our Division. As is evident from the table of contents, there are four definite contributions to the science and art of making pig iron and five valuable papers on stainless steels. Physical metallurgy is well represented by six papers, including an important study of the live subject of the mechanism of austenite decomposition.

Especial attention, however, is directed to the section on steelmaking. In addition to Dr. Herty's interesting and informative lecture on slag control, there are four papers devoted primarily to the physical chemistry of steelmaking and a 44-page condensation of the all-day round table discussion organized by the Physical Chemistry of Steelmaking Committee of the Division. At this round table were discussed frankly such fundamentals as methods of analysis for gases and inclusions, slag-metal and gas-metal reactions and temperature measurements in molten iron and steel, methods for the study of slag composition and characteristics, and the application of these to practical open-hearth problems. The members of the Physical Chemistry of Steelmaking Committee are to be congratulated for their work in organizing the round table, which attracted wide attention and a large audience, and—equally important—for their work in assembling and editing the stenographic notes and putting these in suitable form for publication as a permanent record in the TRANSACTIONS.

F. T. SISCO, *Chairman*,  
Iron and Steel Division.

NEW YORK, N. Y.,  
September 11, 1940.



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THE Howe Memorial Lecture was authorized in April 1923, in memory of Henry Marion Howe, as an annual address to be delivered by invitation under the auspices of the Institute by an individual of recognized and outstanding attainment in the science and practice of iron and steel metallurgy or metallography, chosen by the Board of Directors upon recommendation of the Iron and Steel Division.

So far, only American metallurgists have been invited to deliver the Howe lecture. It is believed that this lecture would gain in importance and significance were it possible to include metallurgists from other countries, but the Institute has not yet been able to do this on account of lack of special funds to support this lectureship.

The titles of the lectures and the lecturers are as follows:

- 1924 What is Steel? By Albert Sauveur.
- 1925 Austenite and Austenitic Steels. By John A. Mathews.
- 1926 Twenty-five Years of Metallography. By William Campbell.
- 1927 Alloy Steels. By Bradley Stoughton.
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- 1938 On the Allotropy of Stainless Steels. By Frederick Mark Becket.
- 1939 Some Things We Don't Know about the Creep of Metals. By H. W. Gillett.
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*Henry Marion Howe Memorial Lecturer, 1940*

## Slag Control

By C. H. HERTY, JR.,\* MEMBER A.I.M.E.

(Henry Marion Howe Memorial Lecture†)

ALMOST every metallurgist who has given the Howe Memorial Lecture has had a personal contact with the distinguished gentleman to whose honor this hour is devoted. Unfortunately for me, such personal contacts were not possible. However, in the preparation of a thesis on the open-hearth process, one of my earliest tasks was to make a survey of the literature, and it was from Professor Howe's Metallurgy of Iron and Steel that I drew a number of references to previous work which formed the foundation for my reading. In his volume there is such a complete exposition of the then current thought on the subject of slags and on their role in the elimination of phosphorus from steel that I feel no hesitation in discussing in this Howe Lecture the subject of "Slag Control."

In the present era of close specification, the drive for uniformity of product, and the close inspection of the product and of the cost sheet, the utmost efforts must be made to control the steelmaking variables to the best advantage of the steel producer. One of the major variables is the slag in the furnace and its effect upon the composition and quality of the metal.

What advantages are to be gained from slag control? In the broad sense the advantages must be tremendous, because the very foundations of good steel melting are based on "shaping up" the slag to a point where, with proper temperature, the heat is ready for the final additions. Every melter works toward these ends through his experience with innumerable heats of steel. The elimination of undesirable constituents such as phosphorus and sulphur is entirely a matter of slag composition and physical nature, a point well known for over half a century. The role played by the slag in assisting in proper heat transfer from roof and flame to the steel has been equally well known. In more recent years there has come the problem of oxygen control in the more accurate gauging of additions for making high-grade rimmed steel for the new strip mills, and in the deoxidizing additions for grain-size control and cleanliness of forging steels, both carbon and alloy. In this problem the oxidizing characteristics of the slag are of prime importance.

\* Research Engineer, Bethlehem Steel Co., Bethlehem, Pa.

† Presented at the New York Meeting, February 1940. Seventeenth Annual Lecture. Manuscript received at the office of the Institute Feb. 16, 1940. Issued as T.P. 1203 in METALS TECHNOLOGY, June 1940.

The present interest in slag control is therefore a result of the desire to take advantage of all possible technical details that will assist the melter in producing a desired grade of steel, to supplement the melter's experience with new technical information and to assist him in translating this information into the most economic practice.

In considering any method of control it is necessary to view critically the costs involved, and balance these against the gains. The costs will include the equipment and the personnel necessary, and any adverse effect of the method on operations. The effort required on the part of the operating staff must also be considered. The gains to be derived may include a decrease in avoidable losses, increase in output, a higher quality, or a more uniform quality. The control method may also provide a better chance to solve questions arising from too great a number of variables operating simultaneously.

### SLAG REACTIONS

Early in the development of our knowledge of slags, rapid strides were made in determining the constituents of the slag that affected the elimination of metalloids, particularly phosphorus and sulphur. The issues of the British Iron and Steel Institute contain a number of articles indicative of the thought that was being put upon the problem of slag-metal reactions in the nineteenth century. As early as 1879 Snelus<sup>1</sup> gave a complete exposition of the use of lime in the elimination of sulphur and in 1885 Vogt<sup>2</sup> found that sulphur was present in the slag as calcium sulphide. Jüptner<sup>3</sup> summarized the reactions controlling sulphur in a most complete manner. It was shown by Osann<sup>4</sup> that high lime and low iron oxide were essential for extensive sulphur removal. He wrote the reaction for sulphur elimination as



the form in which it is usually written today. Our present state of knowledge regarding the elimination of this metalloid has advanced over the views expressed by these authors only in that more quantitative data have been added and that the amount of sulphur in the fuel is now recognized as being highly important.

In the early years of the present century no less than five investigators determined that the phosphorus in the slag was present as tricalcium phosphate,  $3\text{CaO} \cdot \text{P}_2\text{O}_5$ . These early investigators also found that phosphorus could not be readily eliminated unless a considerable amount of FeO was present in the slag.

It was not until more recent years, however, that the general equation for elimination of phosphorus was rather completely understood, and that it was recognized that both excess lime and oxidizing power of the slag

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<sup>1</sup> References are at the end of the paper.



must be considered. The equation for phosphorus elimination is now written as



The effect of temperature on elimination of both phosphorus and sulphur was well understood in practice in the early days of steelmaking, low temperature being used for maximum phosphorus elimination and high temperature for sulphur elimination. Furthermore, the necessity for working with a fluid slag was early recognized. Thus a sound basis had been laid for the proper elimination of phosphorus and sulphur.

Even though the basicity of the slag is of first importance in the elimination of phosphorus and sulphur, we know next to nothing about this important item. The earliest investigators calculated the basicity of the slag by determining the "acidity," the "basic index," the "base acid ratio," or other terms, all of which were simply ratios of the concentrations of basic to acid constituents in the slag expressed in one way or another. Today, we use the lime-silica ratio, which is simply another way of expressing exactly what the earlier investigators had in mind. No one as yet has actually determined how much active lime there is in an open-hearth slag, and until such studies are made the important reactions in the basic open-hearth process must still be considered to be applied by empirical methods.

In recent years the iron oxide content of the metal bath and the reactions of deoxidation have been studied intensively. In rimmed steels we attempt to control the FeO in the metal at a fairly high concentration, in semikilled steels at a fairly low concentration and in killed steels at a very low concentration. The hydrogen reduction method of Ledebur was the earliest proposed for the determination of oxygen in steel and for many years the only one. Later, various other methods were developed; namely, cold acid extraction, hot gaseous extraction, vacuum fusion, electrolytic methods, and, more recently, precipitation of oxygen from steel with aluminum to form  $Al_2O_3$  and the determination of the  $Al_2O_3$  by simple chemical analysis.<sup>5,6,7</sup>

The most recent information attained by the last named method indicates that the controlling factor in the oxygen content of the steel is the carbon content. However, slag oxidation and fluidity have an important bearing on the oxidation of the steel after the furnace deoxidizers are added and on the oxidizing action of the slag on the metal during tapping and in the ladle. Below about 0.10 per cent carbon the iron oxide content of the slag has a more important effect on the oxygen content of the metal than at higher carbons. Last minute changes in the condition of the slag on rimmed heats have a tremendous effect on the rimming action, which shows that carbon alone does not entirely control the oxygen content of the steel.

This point should not be passed without tribute to the work done by Schenck, Körber, Chipman and others who have accumulated a large amount of extremely important data on the whole subject of oxygen and carbon in steel.

Our knowledge of the variables affecting the sulphur, phosphorus and oxygen contents of the metal may be summarized as follows:

*Sulphur.*—The sulphur in the metal is lowered by increased basicity, fluidity, and agitation of the slag and by high temperature. High iron oxide and increased sulphur in the charge (including sulphur absorbed from the fuel) make the attainment of a given sulphur more difficult. The FeO effect is often difficult to observe in practice because high basicity usually causes the slag to be high in FeO.

*Phosphorus.*—The phosphorus in the metal is lowered by increased basicity and fluidity of the slag, a high FeO content of the slag and by low temperatures. High phosphorus in the charge is an adverse factor to the production of low-phosphorus metal.

*Oxygen.*—The oxygen content of the metal before deoxidation is controlled by the carbon in the metal and the FeO content of the slag. Above about 0.10 per cent carbon, the slag is of minor importance, but as the carbon diminishes below 0.10 per cent the slag becomes more important. After deoxidation, particularly in the furnace, the slag composition and fluidity play an important role in determining the oxygen content of the steel. The effect of temperature has not been definitely determined. It increases the solubility of FeO in iron, affects the carbon-iron oxide reaction in the metal, and increases diffusion of iron oxide from slag to metal.

#### SLAG CONTROL

In order to arrive at a desired composition of the metal, with particular respect to sulphur, phosphorus and oxygen, it is necessary to carry a definite type of slag, depending upon the analysis of the raw materials. Slag control is primarily a phrase used to describe the effort to produce this type of slag, be that effort directed toward the open hearth or to the blast furnace. The choice of raw materials entering the blast furnace, with their effect on the composition of the iron, has a definite effect on the slags produced in the open hearth, and constitutes the first step in the control of the open-hearth slag. It is in this phase that the wider aspects of the economics of control first appear in the steelmaking operation. A plant in which the blast furnace is fed with materials that ensure a uniform quality and analysis of pig iron is a tremendous asset to the open hearth from the standpoint of slags, but the analysis chosen for the blast furnace may not be the one best suited for lowest over-all costs, and it is on this point that open-hearth slag control contributes greatly to the economics of steelmaking.

Take, for example, a blast-furnace product containing 0.22 per cent phosphorus and 0.025 per cent sulphur. The open-hearth operator's troubles may be over as far as these two elements in his steel are concerned, but blast-furnace costs may be excessive compared to those when producing an iron containing 0.30 per cent phosphorus and 0.040 per cent sulphur. The intelligent use of a practicable system of slag control in the open hearth will enable the operator to use the iron at a slightly increased cost over that which may be made when using the iron having better analysis. The blast furnace costs, however, will be much lower on the second analysis, and the savings here may well more than balance the extra cost to the open hearth.

### OBJECTS OF SLAG CONTROL

From this discussion on the factors affecting the elimination of metalloids and the desirability for oxygen control, it may be stated that the ultimate objects of slag control should then be:

1. To produce a slag in the furnace that will eliminate phosphorus and sulphur to the desired extent without excessive use of lime or excessive loss of iron as oxide.
2. To conserve as far as possible both lime and deoxidizers.
3. To prevent excessive wastage of iron in the slag, on grades that do not have strict phosphorus requirements.
4. To minimize the melting period through the use of as little limestone in the charge as possible.
5. To standardize the conditions of oxidation so that the deoxidizing additions will unfailingly produce the desired type of ingot.

### OPEN-HEARTH SLAGS

It is obvious to any one versed in basic open-hearth operations that the open-hearth slag is as variable in its behavior as it is interesting in its study. Various amounts of lime are left on the bottom at melt, various amounts of lime are *dissolved* in the slag at melt and various amounts of lime float about in the slag, in one extreme giving the slag a thick, mucky appearance, in the other the impression that huge cakes of ice are floating on a black river. With these variations no one has yet been able to develop methods that permit an *exact* control over the slag composition at any time, and it is necessary to rely upon the laws of probability in seeking our methods of attack.

We can determine experimentally that the lime-silica ratio of the slag is reflected qualitatively in its fluidity, its FeO content, the appearance of a slag cake poured in a definite manner, and in a number of other physical or chemical properties. We also know by experience that the FeO in the slag is building up throughout the refining period at a rate determined



largely by the basicity and the fluidity of the slag. From these qualitative observations we can then say:

1. That early tests give a reasonable idea of the slag qualities of the heat.
2. That the undissolved lime will go into solution in a length of time depending on the composition, fluidity and temperature of the slag.
3. That corrective additions will be assimilated in a reasonably definite length of time and thus influence the build-up of iron oxide in the slag to a certain degree.

If our estimates have been fairly accurate on these three items, we finish the heat with a slag close to the desired composition. Errors in our estimates and vagaries in the behavior of the furnace cause deviations, sometimes more than we would like. However, we know we should attempt to proceed in a certain direction in slag conditioning and the more numerous our signs, and the more rapidly we interpret them and make remedial corrections, the closer we come to our desired end point.

#### EFFECT OF SILICON IN CHARGE

The primary cause of the variations in the working of open-hearth heats is in the variation of the analysis of the pig iron used, and the element that is of first importance in the blast-furnace metal is silicon. A reasonable uniformity in this element is most desirable, be the range 0.60 to 0.90 per cent, or 1.00 to 1.30 per cent. Widespread silicon analyses from cast to cast or from furnace to furnace cause havoc with the melting of the open-hearth heats. The open-hearth furnace is usually charged with limestone before the iron analysis is definitely known, and although the operator can vary his limestone charge to some extent this is seldom practicable because the charges have to be made up for some time before the heat is ready. Furthermore, a furnace cannot take excessive amounts of corrective slag additions without serious interference with heat time. Average heat time is greatly affected when the variation in silicon is sufficient to cause some heats to melt extremely high with attendant long duration of the refining period, generally accompanied by some bottom trouble, and other heats to melt "soft" when they are scheduled to make medium and high-carbon grades.

In a furnace charged with 280,000 lb., the metallic charge consisting of 50 per cent hot metal, 46 per cent scrap, and 4 per cent ore, and with 9 per cent of limestone (based on metallic charge), the percentage of silica in the finishing slag will change with the silicon content of the iron as shown in Table 1.

As the silicon on the hot metal increases, the lime-silica ratio in the open-hearth slag decreases rapidly. Let us assume that a grade of steel is being made that requires a low sulphur content, and that in order to

reach this content a lime-silica ratio of 3.5 is required. In the charge shown in Table 1 a 1.0 per cent Si iron practically fulfills these conditions. With increasing silicon in the hot metal, more stone must be charged, or

TABLE 1.—*Relation between Silicon in Hot Metal and Slag Analysis*

Silicon in Hot Metal, Per Cent	Final Slag Analysis, Per Cent		
	SiO <sub>2</sub>	CaO	Ratio $\frac{\text{CaO}}{\text{SiO}_2}$
0.6	10.3	48.7	4.7
0.8	12.0	47.7	4.0
1.0	13.7	46.8	3.4
1.2	15.3	45.9	3.0
1.4	16.8	45.1	2.7
1.6	18.3	44.3	2.4
1.8	19.7	43.6	2.2
2.0	21.1	42.8	2.0

burnt lime must be added during the working of the heat. The amount of burnt lime required would be as shown in Table 2.

TABLE 2.—*Relation between Silicon in Hot Metal and Lime Required for Correction*

Silicon in Hot Metal, Per Cent	Burnt Lime Required to Give a Lime-silica Ratio of 3.5, Lb.	Silicon in Hot Metal, Per Cent	Burnt Lime Required to Give a Lime-silica Ratio of 3.5, Lb.
0.6	None	1.4	4,800
0.8	None	1.6	7,000
1.0	300	1.8	9,200
1.2	2,500	2.0	11,400

If these additions are to function properly they must be put into the furnace reasonably early so that the CaO may be effective in desulphurization. Heavy additions of this type chill the bath to such an extent that the heat will be delayed and extra costs will be involved in both production and fluxes.

The same principles apply to phosphorus elimination with the added effect of the lime-silica ratio on the behavior of the FeO content of the slag. Thus with high-silicon iron it is not sufficient to add lime only; iron oxide, generally in the form of roll scale, must also be added to raise the iron oxide content to the point where satisfactory phosphorus elimination is assured.

#### CORRECTIVE ADDITIONS

In the examples given in the foregoing pages it is important that when variations in the silicon content of the iron occur the promptest possible

compensating steps be taken. These can be classified as: (1) change in the normal limestone charged, (2) the addition of corrective agents as soon as the hot metal is added, (3) the addition of corrective agents during the melting of the heat, (4) the addition of corrective agents after the heat is melted.

#### CORRECTIONS ON CHARGING

The open-hearth operator is faced with a real problem in varying the limestone charged. This is particularly true if the hot metal comes from more than one furnace. If the silicon does not change to the extent that he has estimated, the furnace may be still undercharged or overcharged with lime. If overcharged, soft melting heats may result, with resultant lengthening out of the heat time in the furnace. This naturally leads to caution in changing the stone charged. Fortunately, most open hearths use a mixer, which to some extent smooths out irregularities in the iron, and this allows for a reasonable change in stone charged, without undue danger.

With close cooperation between the blast furnace and open hearth, and with frequent analyses or calculation of the silicon content of the iron in the mixer, the first step in slag control can be made. This step cuts down the work to be done by corrective additions later in the heat.

The silicon content of the iron is usually known with fair accuracy when the iron is ready for charging in the open hearth. Shortly after the hot metal is added it may be advisable to make an addition of lime in some form in order to compensate for high silicon and from 1000 to 3000 lb. of CaO may be added at this time. In some plants an early addition of lime is made on all heats in order to minimize erosion of the furnace banks by the siliceous slag which forms early in the heat.

#### ESTIMATION OF SLAG COMPOSITION

As the melting of the heat proceeds and lime begins to show in the slag, the true characteristics of the charge begin to be seen. There are a number of indicators, which serve to give a good approximation of slag composition during this period.

First, there is the trained eye of the melter. There are also observers who are conversant with slag characteristics and analyses.

Second, rapid methods of chemical analysis are now available so that the total iron (usually expressed in FeO) may be returned from the laboratory in about ten minutes from the time the sample is taken, with a somewhat longer time required for a silica analysis. Either of these analyses can be of great help if taken at the proper time, the FeO not only for an indication of the state of oxidation of the slag, but as a guide to its silica content. Fig. 1 shows the relationship between FeO and silica in the slag during the lime boil for one open-hearth shop. There is a con-

siderable deviation from this line in practice, but the very definite trend indicates how useful this analysis may be in approximating the silica content of the slag.

Third, there are numerous physical characteristics of the slag, which reflect composition with varying degrees of accuracy. Some of these are immediately apparent to anyone who has carefully watched a heat of basic steel, two characteristics in particular having been widely used by the furnace operators from the earliest days of steel melting. These were the consistency of the slag and the color of slag remaining on the test spoon after the withdrawal of steel samples from the furnace. Tests that will give a better approximation of composition have more recently been developed as the desire for more accurate control has grown, and are particularly useful when a melter has under his guidance too many furnaces to give exclusive attention to any one, especially during the early periods of the heat.

*Appearance of Slag in Furnace.*—The appearance of the slag in the furnace during the melting period is indicative of its composition and of its future requirements. Charges too high in silicon will show a thin, watery slag, usually low in iron oxide, and with numerous lumps of lime apparently indifferent to the laws of solution. Research with the

petrographic microscope has shown that these lumps are coated with a high-melting-point layer of dicalcium silicate, which can be fluxed away only by the action of fairly high concentrations of iron oxide or spar in the fluid slag. Charges too low in silicon result in a slag thick with lime, with very small amounts of fluid slag observable. Such slags are generally of medium or high iron oxide content, and are easily "shaped up" by additions of roll scale, fluorspar, or sand. (Pioneer work on the advisability of making acidic additions to the open-hearth heat was begun by Cook<sup>3</sup> as early as 1928.) How much of any addition should be made is a question of personal judgment and the success of the slag conditioning depends entirely on the skill and experience of the melter.

*Color of Slag.*—The color of the slag when cooled in water is a guide to its approximate composition. Slag color has one definite advantage

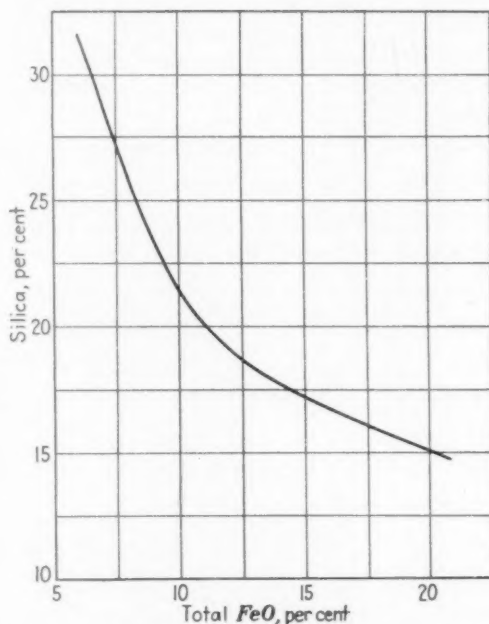


FIG. 1.—GENERAL RELATIONSHIP BETWEEN SILICA AND TOTAL IRON OXIDE IN SLAG DURING MELTING.



in that a review of any period of the heat may be made if samples have been taken over that period. A melter who is busy tapping "No. 5" may not have had an opportunity to take a look at "No. 1" during its melting period, but a set of slag samples will give him a good idea of the course of events during melting. Slag color and composition may be grouped roughly as shown in Table 3.

TABLE 3.—*Slag Color and Composition*

Color	FeO	CaO/SiO <sub>2</sub> Ratio
Black.....	Medium	Low
Gray.....	Low	Low
Light brown.....	Medium	Medium
Dark brown.....	Medium	High
Chocolate brown.....	High	High

*Slag Cakes.*—The appearance of the surface texture of slag cakes poured into standard molds is an interesting and, in many plants, a useful guide. This method was first proposed in this country by Janitsky.<sup>9</sup> The surface of a slag cake changes from a wrinkled, sometimes crepelike top in a weakly basic slag to a shiny, smooth top in a more basic slag, and finally to a lusterless top in an extremely basic slag. Surface markings resulting from high MnO and high P<sub>2</sub>O<sub>5</sub> give useful information on the working of the slag with respect to elimination of manganese and phosphorus. Melters and observers must, and can, be trained in slag-cake reading, and the results obtained are naturally influenced by the personal factor involved. Changes in raw materials affect the appearance of the cakes, hence a given interpretation in one shop may not be applicable to some other shop.

*Slag Viscosity.*—Another useful characteristic is slag viscosity, which has been long used by acid-open-hearth melters as a criterion of slag condition. In this instance the manner in which the slag flows off a stirring rod after withdrawal from the furnace is used as the melter's guide. For basic slags the viscosity is usually determined by the flow of slag in a tube as developed in the work of the Metallurgical Advisory Board in Pittsburgh (Physical Chemistry of Steel Making, 1934). In this method the length of flow actually measures a combination of slag fluidity, the reciprocal of viscosity, and melting point. In sampling the slag a test spoonful is cast into the measuring instrument (Fig. 2) and the length of flow is measured by a rod inserted in the open end (Fig. 3). Care must be taken in casting the slag quickly, for the fluidity of certain types of slag is sensitive to temperature drop. The general relationship between slag fluidity as measured by this method and the lime-silica ratio is shown in Fig. 4. Changes in raw materials in the charge may shift the position of this curve slightly.

One objection to this method is that slag temperature will affect the flow, and this is undoubtedly true in extreme cases. The use of fluidity measurements as indicators of slag composition is limited to slags to which no fluorspar has been added.



2



3

FIG. 2.—CASTING SLAG INTO VISCOSIMETER.

FIG. 3.—MEASURING SLAG FLOW IN VISCOSIMETER.

*Other Methods.*—In the last few years much thought has been given to new methods of measuring slag composition by quick methods. Among these are magnetic characteristics, density, electrical conductivity measurements and the use of the petrographic microscope, but none of these has as yet reached the point where it has been put into practice as a control method.

## CORRECTIONS DURING WORKING

Having described various methods of judging slag composition, we now come to the question of how to use them. The most obvious method is to turn them over to the melter and allow him to use them to supplement his knowledge in preparing the heat. In addition to this, there is further information to be gained by the study of sufficient heats to determine the average behavior of various grades of steel in respect to changes in slags and the effect of these changes on the metal.

The general principle of utilizing information obtained during the melting of the heat is simple. For any given grade we desire a certain type of finishing slag. From experience, which of course includes correlation of operating and test data, it is known that the more acid a

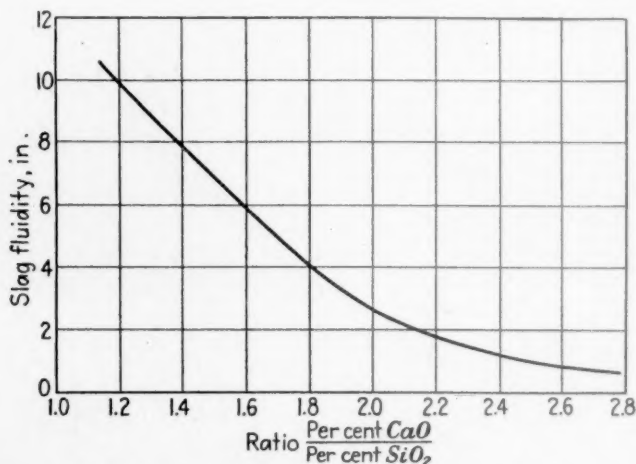


FIG. 4.—GENERAL RELATIONSHIP BETWEEN SLAG FLUIDITY AND BASICITY DURING MELTING.

slag during melting, the larger the quantity of lime necessary to arrive at a given basicity. Also, if the early slags are excessively low in iron oxide, the normal build-up of iron oxide in the slag during the refining period may not be sufficient to give a slag of the desired iron oxide content at the end of the heat, the desired iron oxide content being controlled by the amount necessary to satisfactorily eliminate phosphorus, accelerate carbon elimination at low carbon contents, or promote the proper action in the molds of rimmed-steel heats. If the slag is excessively basic during the melting period, large amounts of expensive fluidifying agents may be needed and the finishing slags may be higher than necessary in iron oxide, thus causing a loss of yield of iron and unnecessarily large additions of deoxidizing agents.

With these factors in mind, Fig. 5 shows the procedure that should be followed, based on tests taken during the melting period. This figure shows the iron oxide content in the slag plotted against any slag property

that indicates acidity. On the chart are shown four zones, in each of which certain additions are indicated:

1. If the slag is high in iron oxide and quite basic, the addition of an acid constituent may be indicated, depending on the grade of steel being made. This acid addition will avoid the use of excessive amounts of fluorspar and will assist in keeping the iron oxide content of the slag in the desired range.

2. In another range of slag acidity and FeO, the heat will finish with the desired slag with no additions. This zone naturally will shift on the chart, depending on the grade of steel being made.

3. If the slag is exceedingly acid and reasonably low in iron oxide, a basic addition is indicated, which will give the desired lime-silica ratio at the end of the heat and assist in raising the iron oxide content of the slag in refining.

4. If the slag is extremely low in iron oxide it may be necessary to make an addition of oxide to the slag, and usually to make this addition in conjunction with a basic addition.

Obviously, the amounts of these additions will depend on the degree of acidity and on the percentage of FeO in any particular zone.

Experience in charting the various slag properties indicating acidity and the percentage iron oxide in the slag allows such charts to be set up, so that by the time the refining period is under way most of the corrective additions will have been made and assimilated in the slag. The advantage of making additions at melt or as soon after as possible is that there is little danger of such additions being undissolved in the slag at the time of tap, and thus reaping the benefits of the additions to the fullest possible extent.

If the heat has been successfully made up to the time the refining period starts, and if the proper steps have been taken to correct the charge and the early slags, the only corrective addition made during refining will be additions of lime to compensate for the silica in the ore added for carbon elimination. However, as a check on the condition of the heat after the slag has begun to shape up, usually tests are taken, which will indicate again the lime-silica ratio of the slag and its iron oxide content. At this time fluidity tests are sometimes of little value because fluorspar may have been added. Slag cakes, slag color and analyses of slag and metal now serve as the best guides toward slag composition and the necessity for further additions. The disadvantage

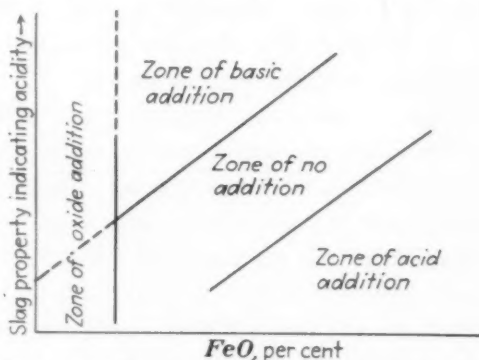


FIG. 5.—CORRECTION CHART FOR BASIC OPEN-HEARTH SLAGS.



of slag analysis during this period is that with a fast working heat the analyses may not be returned in time to allow corrective additions to function properly before the heat is ready to be tapped. However, such analyses, together with the taking of slag cakes and color samples, usually prove valuable in the final adjustment of the slag to its desired composition. The common additions during this period of the heat are burnt lime for increasing basicity and roll scale for increasing the iron oxide content of the slag.

### MODIFICATIONS AND APPLICATIONS

To illustrate modifications and applications of the procedures described in the previous pages, three examples have been chosen of control methods for sulphur, phosphorus and iron oxide in the slag.

*Sulphur.*—The factors affecting elimination of sulphur have been discussed earlier in the paper. One of these was the sulphur in the charge. This is an unknown factor at the time the heat is under cover if the furnace gases carry sufficient sulphur to give an appreciable sulphur pickup by the scrap. Furthermore, at the time of melt it is very difficult to say just how much sulphur will be eliminated from melt to tap. But this much we do know; that the higher the sulphur in the metal at melt, the more work we must do to lower it to a given content. Therefore it seems reasonable to take a sulphur test early in the heat and make an additional adjustment of the slag as may be indicated. There is no straight-line relationship between the sulphur during the melting period and the sulphur at tap, but the chances of low sulphur at tap are better with low than with high sulphur at melt. Hence we are working in the right direction if we take an early sulphur and add lime as soon as possible if this test shows high sulphur. This can be put on a common sense basis by knowing the general relationship between the early sulphur and the ladle sulphur and adding lime accordingly. For example, if the sulphur test is taken about an hour before melt, it may very well be that the following relations will be found:

Sulphur 1 Hour before Melt	Ladle Sulphur to be Made	Extra Additions Needed
0.040	0.030	None
0.050	0.030	1 box lime
0.060	0.030	3 boxes lime

This system has been used to good advantage in many plants and is of particular assistance where the diversion of heats for high sulphur, or the working of heats for longer than average time, is excessive.

*Phosphorus.*—An interesting example of the utility of slag control is found in the records of a plant making a considerable tonnage of carbon

steels in the range 0.35 to 0.50 carbon. One of the desired qualities in this particular grade was that the ladle phosphorus should not exceed 0.025 per cent. It has been demonstrated earlier in this paper that the controlling factors in phosphorus content of the finished steel are basicity, iron oxide content,  $P_2O_5$  content of the slag, and temperature. Lacking complete slag analyses, the basicity may be roughly judged by the FeO content of the slag, the latter generally decreasing with decreasing basicity.

This grade of steel was made over an extended period with no definite slag-control schedule and 22 per cent of the heats finished higher in phosphorus than specified to the open hearth. A survey of these heats showed an interesting relationship between the  $P_2O_5$  of a preliminary slag and FeO content of the tap slag (Fig. 6). In this figure the percentage of high-phosphorus heats is shown in the various analysis zones.

On the basis of these data the phosphorus content of the iron was lowered slightly and a slag-control schedule was put into effect, which gave the melter the  $P_2O_5$  and FeO contents of the slag shortly after melt, with suggested additions for increasing the FeO and CaO content, depending on the analyses. A two-months run on these schedules resulted in only

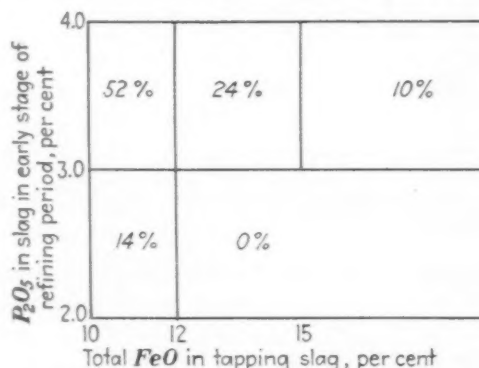


FIG. 6.—RELATION BETWEEN PERCENTAGE OF HIGH-PHOSPHORUS HEATS AND SLAG ANALYSIS.

3 per cent of the heats above the limit specified to the open hearth. The percentage of heats with more than 3.0 per cent  $P_2O_5$  decreased from 77 to 30, and the percentage of high-phosphorus heats in the upper brackets decreased from 27 to 9, in the lower brackets from 3 to 1. Had the iron been changed with no slag-control schedule, the percentage of high-phosphorus heats would have been 9.5. With the same iron and slag control the percentage would have been 7.1; with both operating simultaneously the percentage was 3.0.

The optimum cost to the plant in this case can easily be calculated by correlating the decreased value of the high-phosphorus heats, the cost of the two types of pig iron and the costs of the extra additions made necessary by the slag-control schedules.

*Iron Oxide in Slag.*—In controlling the FeO content of the slag it is generally advisable, in making killed steels, to carry as low an FeO as is consistent with reasonable elimination of phosphorus. High oxide contents result in loss of iron in the slag.

One factor that intrigues the writer is that occasionally a certain furnace will, for some unknown reason, become an individualist with

respect to FeO content and refuse to go along with the other furnaces in the shop. An excellent illustration occurred in a shop making killed steel and operating three furnaces, the three being at one end of a rather

TABLE 4.—*Total FeO Content of Finishing Slags on Three Furnaces*  
Asterisks Show Slags over 16 Per Cent FeO

Furnace No. ....	42	43	44
	11	14	13
	19*	13	18*
	20*	13	16
	14	13	14
	13	16	11
	12	13	12
	15	14	16
	18*	13	19*
	17*	16	16
	17*	14	20*
	12	16	12
	16	9	13
	13	13	15
	13	13	13
	18*	14	15
	17*	12	14
	17*	14	14
	19*	12	18*
	17*	10	17*
	19*	15	15
Slag Control Schedule Changed on Furnace No. 42			
	15	10	12
	12	16	13
	15	14	16
	17*	15	15
	13	15	20*
	13	18*	19*
	13	18*	16
	15	16	16
	16	17*	15
	12	13	15
	13	12	13
	13	12	14
	13	11	16
	13	11	10
	11	13	13

long shop. All were on the same slag-control schedules and one day it was noted that the percentage of high FeO heats had been gradually increasing and the particular system in vogue seemed to be out of order.

A quick survey of the last 20 heats made on each furnace showed the following most interesting figures:

Furnace No.....	42	43	44
Percentage of heats under 16 FeO.....	45	100	75
Percentage of heats over 16 FeO.....	55	0	25

Seventy per cent of all the high iron oxide heats were on one furnace, and this furnace was immediately put on a special schedule of its own. The results of the following week's operation were:

Furnace No.....	42	43	44
Percentage heats under 16 FeO.....	94	80	87
Percentage of heats over 16 FeO.....	6	20	13

Here was a definite proof that a furnace characteristic was controlling the type of slag produced, but that a proper diet for that furnace could make it fall in line with its sisters. Table 4 shows the FeO content of the tapping slags on the three furnaces during this period.

#### CONCLUSION

There is yet much to be learned about slags and their effects on the metal. Fundamental research on slags, particularly on the real meaning of basicity, may open new fields of activity and new methods of approach to the steel-melting problem.

Nevertheless, we believe that slag control has become an integral part of the open-hearth activities from charge to tap, and that the benefits to be derived are sufficient to warrant its extended use. No set rules can be laid down for all conditions of operation because requirements and raw materials necessarily affect the degrees to which control must be exercised.

Finally, in any development that must fit into the operations of an open-hearth furnace, the words of Réaumur should be noted well. This eighteenth century steelmaker and research worker put the problem of the application of cementation into the words, "It is necessary to have this art known and easy to practice by workmen." Slag control is no exception to this statement.

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## Effect of the Solution-loss Reactions on Blast-furnace Efficiency

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(Cleveland Meeting, April 1939)

SHORTLY after the middle of the nineteenth century, the invention of the regenerative open-hearth furnace and the development of the Bessemer process stimulated a rate of steel production whose magnitude created an unprecedented demand for pig iron.

Revolutionary improvements in furnace design, auxiliary equipment, and operating technique enabled the blast furnace to keep abreast of the constantly increasing requirements of the steel mill. The development of improved blowing equipment, more adequate facilities for material handling, and particularly the general use of anthracite and coke to replace the physically weaker charcoal, led to a rapid expansion in both the height and volume of furnaces.

Beyond a doubt, however, the greatest single factor in blast-furnace improvement at this time was the use of the higher blast temperatures made available by the replacement of the recuperative iron pipe stoves by the regenerative Cowper brick stove. The increased blast temperature not only resulted in greater output but also reduced fuel consumption far more than could be explained by the additional heat content of the blast.

The progress of iron manufacturing was thus largely mechanical and thermal. Little attention was given the chemistry of the process until the publication of the investigations of Sir Lowthian Bell.<sup>1</sup> Bell's painstaking experiments and investigations gave to the blast-furnace man his first real scientific conception of blast-furnace chemistry. Bell's recognition of the dual function of the carbon, the technical importance of reversible reactions and chemical equilibria, and his conception of the degree of oxidation of the carbon as shown by the analysis of the outgoing gases as a criterion of furnace efficiency, laid the foundation upon which has since been erected the structure of blast-furnace theory.

Prominent among those availing themselves of Bell's data as a basis of further study was M. L. Gruner,<sup>2</sup> professor of the French School of Mines. His "Blast Furnace Phenomena," published in 1870, presented

Manuscript received at the office of the Institute May 2, 1939. Issued as T.P. 1107 in METALS TECHNOLOGY, September 1939.

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<sup>1</sup> References are at the end of the paper.

a new criterion of blast-furnace efficiency called "The Ideally Perfect Working of the Blast Furnace," now known more generally as simply "Gruner's theorem."

The favorable response with which Gruner's conception of the ideal furnace working was received has been little affected by the passing of more than half a century. One need only glance through blast-furnace literature, even of recent date, to discover that an almost axiomatic regard for this principle exerts a tremendous influence upon operators and theorists alike.

So indoctrinated has the industry become with the truth of Gruner's theorem that a special name has been assigned reactions that violate Gruner's principle. These reactions are grouped together under the common term "solution-loss reactions," the very implication of which is that they represent a loss to the furnace process.

J. E. Johnson, Jr.,<sup>3</sup> one of the pioneers of scientific blast-furnace thought in America, devoted pages in his book to his efforts to prove the truth of Gruner's theorem. No doubt the high regard with which the principle has been held in America is due in large part to the stand taken by this eminent author.

Certain writers have questioned the truth of Gruner's theorem. Professor Richards<sup>4</sup> showed clearly that under certain favorable conditions furnace efficiency would be improved by as great a departure from Gruner's principle as possible. Howland<sup>5</sup> made an interesting study of the use of carbon in 26 furnaces based solely on their operating results. He showed clearly that the furnaces of his time, which produced the lowest coke practice, violated Gruner's principle. More recently, Brewster<sup>6</sup> and Austin<sup>7</sup> indicated that furnace performance in certain instances may be improved by violation of Gruner's theorem.

Because of the apparent need for a comprehensive investigation of the many factors entering this controversial subject and particularly because even a brief examination of Gruner's calculations reveals that they fail to conform to the laws of thermochemistry, the following study was undertaken.

#### GRUNER'S THEOREM

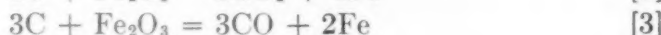
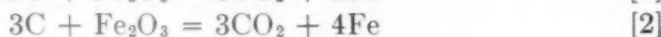
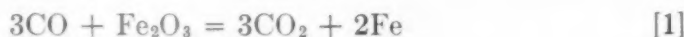
In the English translation of Gruner's book, by L. D. B. Gordon, published in 1874, the ideal working of the blast furnace is expressed in the following terms:

It is therefore of importance that the reduction of ores in the blast furnace should be effected as far as possible . . . by the carbon monoxide being transformed into carbon dioxide or, in other words, without the consumption of solid carbon. This is what we shall allude to in the future as the ideally perfect working of the blast furnace. . . . The carbon monoxide produced near the tuyeres will reduce the ores and be transformed into carbon dioxide, and this in turn will leave the furnace without reaction on the solid carbon. In this case all of the carbon of the charge will pass

through the furnace without other alteration than a gradual heating and this carbon will be finally burned to carbon monoxide under the action of the blast of the tuyeres.

Gruner was led to these conclusions by a series of very interesting theoretical calculations. Since they occupy several pages in the original volume, his calculations will be presented here in a form which, although abridged, nevertheless is faithful to the original thought.

As his basic hypothesis, Gruner states that there are three ways by which iron ores may be reduced by carbon. These are represented by the following equations:



From the heats of formation, Gruner then derives the thermal results of each of these reactions.

In these calculations, the following heats of formation, from Hougen and Watson's Industrial Chemical Calculations, are used:

Heat of formation  $\text{Fe}_2\text{O}_3$  = 3,080 B.t.u. per lb. Fe

Heat of formation CO = 4,400 B.t.u. per lb. C

Heat of formation  $\text{CO}_2$  = 14,550 B.t.u. per lb. C

Heat of formation CO:  $\text{CO}_2$  = 10,150 B.t.u. per lb. C

In the first instance:



the production of one pound of iron will require:

$$\frac{3 \times 12}{2 \times 56} = 0.321 \text{ lb. of carbon as monoxide.}$$

The thermal effect of this reaction per pound of iron produced will be:

Heat of combustion 0.321 lb. C in CO to  $\text{CO}_2$ :

$$0.321 \times 10,150 = 3260 \text{ B.t.u. per lb. Fe}$$

Minus heat of decomposition:

$$\text{Fe}_2\text{O}_3 = -3080 \text{ B.t.u. per lb. Fe}$$

Resulting in a credit to the process of:

$$+180 \text{ B.t.u. per lb. Fe}$$

The heat of reaction No. 2 is calculated as follows:



To produce one pound of iron requires:

$$\frac{3 \times 12}{2 \times 2 \times 56} = 0.1605 \text{ lb. C}$$



The thermal effect of the reaction of 0.1605 lb. C to form 1 lb. Fe by this process will be:

Heat of formation of  $\text{CO}_2$  from this amount of C is:

$$0.1605 \times 14,550 = 2335 \text{ B.t.u.}$$

$$\text{Heat of decomposition } \text{Fe}_2\text{O}_3 = -3080 \text{ B.t.u.}$$

$$\underline{\hspace{1.5cm}} \\ - 745 \text{ B.t.u.}$$

which represents a heat deficiency of 745 B.t.u. per lb. Fe reduced.

In a similar manner, the heat effect of process No. 3 is calculated:

As in process No. 1, the reduction of 1 lb. Fe requires:

$$\frac{3 \times 12}{2 \times 56} = 0.321 \text{ lb. C}$$

The heat of this reaction will be:

Heat of formation of CO from 0.321 lb. C:

$$0.321 \times 4450 = 1428 \text{ B.t.u.}$$

Heat of decomposition:

$$\text{Fe}_2\text{O}_3 = -3080 \text{ B.t.u.}$$

$$\underline{\hspace{1.5cm}} \\ -1652 \text{ B.t.u. per lb. Fe reduced,}$$

which again results in a heat deficit, in this case amounting to 1652 B.t.u. per pound Fe. The results in tabulated form are given in Table 1.

TABLE 1.—*Calculations from Gruner's Theorem*

Reaction	Reactant	Pounds Carbon per Pound Fe	Heat of Reaction, B.t.u.	Gas Formed
No. 1.....	CO	0.321	180	$\text{CO}_2$
No. 2.....	C	0.1605	- 745	$\text{CO}_2$
No. 3.....	C	0.321	-1652	CO

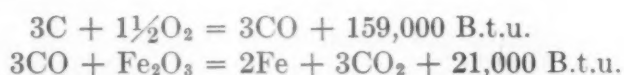
These calculations demonstrate that reaction No. 1 is exothermic, the heat effect of the reaction being a credit of plus 180 B.t.u. per lb. Fe. Reactions 2 and 3, however, are endothermic, each requiring a supply of heat from an external source. From this observation Gruner reasoned that since no heat is furnished to the process when the iron oxide is reduced by the carbon monoxide, and since the reduction by solid carbon requires the supply of heat from a source external to the reaction, the reduction by carbon monoxide must be the most efficient. If the reduction by CO is most efficient, then, concluded Gruner, any reaction involving solid carbon before it is oxidized to monoxide by the air blast must lower the furnace efficiency.

Closer study of Table 1, however, reveals discrepancies, which entirely destroy the value of the comparison. Gruner based his conclusions solely on the thermal effect of the reactions as written. He gave no consideration whatsoever to the fact that in reaction No. 2 only one-half as much carbon is used to reduce a pound of iron as in reaction No. 1. He likewise gave no thought to the fact that in reaction No. 3 the end product of the oxidation of the carbon is only the monoxide, which may then undergo reaction No. 1 and reduce more iron by oxidation of the monoxide to the dioxide. Likewise, in process No. 1, he neglected to consider the fact that, at least as far as the blast furnace is concerned, the formation of the monoxide itself is a part of the process and must be so considered. It is necessary to give proper consideration to these conditions in order that the comparison may be just.

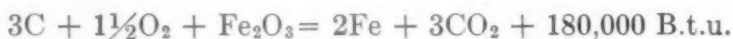
Consequently, we shall revise Gruner's calculations on the basis of starting with the same amount of identical reactants and ending with equal amounts of end products, allowing, however, the reactions to proceed in different ways to test whether there are any essential differences in the various modes of reduction.

To equation No. 1, a correction must be made which compensates for the formation of the reducing agent, carbon monoxide. In the following reactions the modern pound mol unit will supplant Gruner's pound unit.

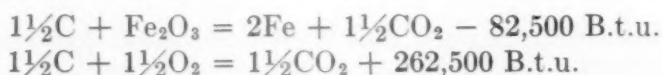
Reaction No. 1 must then be written:



The whole process then becomes:



Reaction No. 2 must be revised to use an equal amount of carbon per unit Fe reduced as reaction No. 1:



And the reaction that expresses the process becomes:



In similar fashion, the proper corrections may be made to process No. 3 and identically the same equation derived as is obtained by making the proper compensations to reactions No. 1 and No. 2.

It is apparent from these equations that there is no difference in the theoretical efficiency of the process, no matter how it is carried out, when the proper corrections are made to Gruner's basic calculations. This is what physical chemistry teaches us to expect, for Hess's Law of Constant Heat Summation states that as long as the initial reactants and final end products are identical, regardless of the manner in which the reaction proceeds, the heat effect is identical.

The error that Gruner made is not uncommon in thermochemical discussions. Frequently, reference is made to the harmful effect of an isolated endothermic reaction without consideration of the over-all results. The effect of variation in an isolated portion of a thermochemical system cannot be compared without consideration of the resultant effect on the entire system.

In formulating a rule applying to the behavior of an entire thermochemical system from consideration of merely an isolated portion of the system, Gruner failed to conform to the laws of thermochemistry and thereby arrived at an erroneous conclusion.

From practical considerations, the objection may be made that the correction made to reaction No. 2 cannot possibly be accomplished in the blast furnace, as carbon cannot be burned to carbon dioxide by the air blast at the tuyeres. That objection is true. It is also true, however, as Gruner states in his book, but neglects to consider in this theory, that reaction No. 1 cannot be effected as written by Gruner; for, just as the existence of  $\text{CO}_2$  at the tuyeres is prevented by the equilibrium relations in the carbon-oxygen system, so also is the extent to which carbon monoxide may be oxidized by iron oxide limited by the equilibrium relations in the iron-carbon-oxygen system. Gruner's failure to give proper consideration to these equilibrium relationships, which set definite limits on furnace performance, is an additional reason why his theory cannot serve as a practical or theoretical criterion of furnace efficiency.

#### LIMITING RATIOS OF CARBON MONOXIDE AND CARBON DIOXIDE IN THE BLAST FURNACE

That the reaction between iron oxide and carbon gases is reversible has been known for many years. Both Bell and Gruner were aware of the fact that when certain proportions of carbon dioxide existed in a mixture of carbon monoxide and dioxide the gas lost its power to reduce iron oxide, and might even reoxidize iron already reduced. The results of investigations into the equilibria between the various oxides of iron and those of carbon are shown in Fig. 1, which is taken from Austin's paper on Blast-furnace Efficiency. It is apparent from this diagram that reduction of iron from its oxides may proceed only when the ratio of  $\text{CO}:\text{CO}_2$  in the gases is greater than 49:51, or 0.96. This, then, is the

limiting ratio, which the composition of the top gases cannot exceed and still retain reducing properties.

The problem of determining the extent to which carbon may be oxidized in the furnace is not, however, so simply solved. It is complicated by the fact that carbon dioxide is produced by the calcination of the limestone. Whatever carbon dioxide comes from this source reduces the amount of dioxide that may be formed from the carbon by an equal

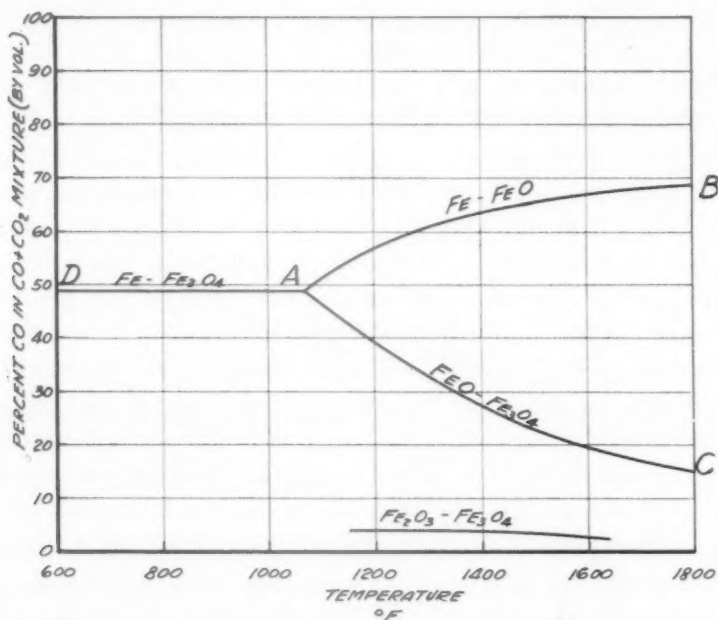


FIG. 1.—PERCENTAGES OF CARBON MONOXIDE IN MIXTURES OF THE MONOXIDE AND DIOXIDE. (From J. B. Austin.<sup>7</sup>)

amount. Consequently, the limiting ratio of  $\text{CO}:\text{CO}_2$  in the gases from the fuel carbon only must be revised to compensate for the limestone calcination. The revised limiting ratio may be calculated from the following equation:

$$\frac{(\text{CO})_f}{(\text{CO}_2)_f + (\text{CO}_2)_s} = 0.96$$

where  $(\text{CO})_f$  = CO resulting from oxidation of fuel carbon

$(\text{CO}_2)_f$  =  $\text{CO}_2$  resulting from oxidation of fuel carbon

$(\text{CO}_2)_s$  =  $\text{CO}_2$  resulting from calcination of limestone

To solve this equation the following assumptions, which are representative of Lake ore practice, will be made:

Coke rate = 1750 lb. coke per ton pig,

Carbon in coke = 89 per cent,

Carbon in iron = 4.25 per cent,

Limestone per ton iron = 700 lb.,

Carbon dioxide content of limestone = 44 per cent.

The actual limiting ratio of the furnace gases produced by the oxidation of the carbon may then be calculated as follows:

1. Carbon supplied by coke =  $1750 \times (0.89) = 1557$  lb.
2. Carbon to pig iron =  $2240 \times 0.0425 = 95$  lb.
3. Carbon available as fuel =  $1557 - 95 = 1462$  lb. or  $\frac{1462}{12} = 121.8$  lb. mols.
4. Mols of CO + CO<sub>2</sub> resulting from oxidation of fuel carbon = 121.8.
5. CO<sub>2</sub> supplied by calcination of limestone =  $\frac{700 \times 0.44}{44} = 7.0$  lb. mols.

Substitution of these results in the two equations:

$$0.96 = \frac{(\text{CO})_f}{(\text{CO}_2)_f + (\text{CO})_f}$$

$$(\text{CO})_f + (\text{CO}_2)_f = 121.8$$

yields

$$(\text{CO})_f = 63.0 \text{ mols}$$

$$(\text{CO}_2)_f = 58.6 \text{ mols}$$

thus bringing the limiting ratio of the gases from the fuel carbon only to:

$$\frac{63.0}{58.6} = 1.08$$

The variation of this limiting ratio, with variations in coke and stone rates, is indicated in Table 2. The ratios were calculated in a manner similar to that shown above.

TABLE 2.—*Variation of Limiting Ratio*

Coke, Lb. per Ton Pig	Limiting Ratio CO:CO <sub>2</sub>		
	With 500 Lb. Stone per Ton Pig	With 700 Lb. Stone per Ton Pig	With 900 Lb. Stone per Ton Pig
1,600	1.05	1.09	1.12
1,750	1.04	1.08	1.11
1,900	1.03	1.07	1.10

In subsequent calculations, a limiting ratio of 1.08 CO:CO<sub>2</sub> will be used. This is the limit to which the monoxide from the fuel carbon may be oxidized to dioxide and still retain the minimum CO:CO<sub>2</sub> ratio of 0.96 in the top gases when the coke rate is 1750 and 700 lb. of limestone are charged per ton of product.

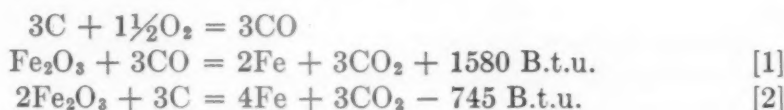
#### THEORETICAL EQUATIONS OF REDUCTION

Since Gruner's theorem does not conform to the laws of modern thermochemistry, it is necessary to study the reduction processes in



greater detail in order to determine whether any chemical or thermal relations exist that make one mode of reduction preferable to the others.

Consideration of the following reactions



demonstrates that each has a superiority over the other, but the superiority is in different respects. Reaction No. 1, as we have shown, is exothermic, generating more heat than can be used by the process. Reaction No. 2 is endothermic, requiring heat from other sources for its progress. Process No. 1, on the other hand, requires more carbon for purely reduction purposes than does process No. 2 because the carbon in reaction No. 2 absorbs all of its oxygen from the ore, while in reaction No. 1 the first atom of oxygen is added to the carbon from the air blast. It is practically self-evident that these reactions can be mutually beneficial; the excess heat developed by reaction No. 1 being used to furnish the heat necessary to promote reaction No. 2, thereby combining the benefits of the exothermicity of reaction No. 1 with the lower reduction carbon required for reaction No. 2, with the ultimate result of minimizing the carbon requirement of the process.

The extent to which this mutual interaction can be helpful is definitely limited by thermal and chemical considerations of the process as a whole. Thermally, the limit is set by the minimum heat necessary for the production of a unit of metal within the furnace; chemically, the limit is set by the minimum CO:CO<sub>2</sub> ratio required in the top gases.

Giving due consideration to the limiting factors, the following series of calculations illustrates the extent to which mutual interaction of the two types of reduction by carbon can be utilized with beneficial results in the blast furnace.

#### 100 PER CENT INDIRECT REDUCTION

A general equation for the iron oxide reducing function of carbon within the blast furnace may be written as follows:



For 100 per cent indirect reduction, the coefficients of the equation must satisfy the following conditions:

1. That all of the fuel carbon is oxidized to carbon monoxide at the tuyeres.

2. That the limiting ratio of the oxides of the fuel carbon is 1.08 CO:CO<sub>2</sub>.

Since the basic equation contains four unknowns, four simultaneous equations must be established to obtain the proper constants. Such

a series of relationships between the numerical coefficients may be set up as follows:

*Carbon balance*,  $(w) = 2(a)$

$$(w) = (b) + (d)$$

*Oxygen balance*,  $2(a) + 3 = (b) + 2(d)$

*Limiting gas ratio*,  $(b) = 1.08 (d)$

Solution of these equations yields the following values:  $w = 6.24$  mols C,  $a = 3.12$  mols  $O_2$ ,  $b = 3.24$  mols CO,  $d = 3.00$  mols  $CO_2$ .

Substituting these coefficients, the basic equation, satisfying the requirements for 100 per cent indirect reduction and a 1.08 CO:CO<sub>2</sub> ratio is:



Using heats of formation, converted into English units from the metric units of the International Critical Tables, the heat effect of the above reaction is calculated as follows:

$$H + 6.24(O) + 3.12(O) + 1(345,000) = 2(O) + 3.24(53,000) + 3.00(175,000)$$

$$H + 345,000 = 697,000$$

$$H = +352,000 \text{ B.t.u. per lb. mol } Fe_2O_3$$

from which it may be concluded that the heat produced by the products of this equation is over twice as great as the heat required for the reduction of the iron oxide.

#### HEAT BALANCE OF THE BLAST FURNACE

The most accurate work on the heat requirements of modern American blast-furnace practice is contained in a paper by Mathesius<sup>9</sup> in 1915, from which the figures of Table 3 are taken.

The total heat requirement for all the work of the furnace per ton of iron produced is shown as 12,848,000 B.t.u. The heat used for the reduction of the iron oxides alone amounts to 6,623,300 B.t.u. From this balance, the conclusion may be drawn that the total heat requirement of

the furnace process is  $\frac{12,848,000}{6,623,300} = 1.94$  times the quantity of heat required for the reduction of the ore alone. In this, as well as all subsequent calculations, the assumption is made that the oxide is entirely  $Fe_2O_3$ . Thus the heat requirement of reducing a pound mole of iron ore in the blast furnace under the conditions of practice described in Mathesius' paper, which are representative of Lake ore practice, is 1.94 times the heat of formation per pound mole of the oxide, or:

$$1.94 \times 345,000 = 670,000 \text{ B.t.u.}$$

The heat effect of the product side of equation No. 1 amounts to 697,000 B.t.u. per pound mol of  $Fe_2O_3$ . Since this is in excess of the 670,000

TABLE 3.—*Heat Requirements of Blast Furnace*

	B.t.u.	Per Cent
Reduction of $\text{Fe}_2\text{O}_3$ 6,133,300		
Reduction of $\text{Fe}_3\text{O}_4$ 490,000		
	6,623,300	
Reduction of $\text{MnO}$ 48,400		
Reduction of $\text{P}_2\text{O}_5$ 17,000		
Reduction of $\text{SiO}_2$ 418,500	7,107,200	55.3
Calcination of carbonates.....	702,000	5.5
Dissociation of moisture in blast.....	397,000	3.1
Carried off with iron.....	1,142,500	8.9
Carried off with slag.....	909,000	7.1
Carried off with dry top gases.....	752,400	5.9
Carried off with moisture in top gases.....	700,000	5.4
Radiation, cooling water and unaccounted for.....	1,137,800	8.8
Total.....	12,848,000	100.0

B.t.u. required by the blast furnace for the industrial reduction of a pound mol of iron oxide, it is evident that a process where the reduction is entirely indirect is self-sustaining from a thermal point of view. Consequently, a 100 per cent indirect reduction process can avail itself of no heat from an external source. Under such conditions, no blast heat need be used and none of the waste heat chemically available in the top gases may be advantageously returned to the process. The theoretical coke rate of such a practice under the following assumptions

Carbon content of coke = 89 per cent  
 Fe content of one ton of pig = 2097 lb.  
 Carbon content of pig = 4.25 per cent

would be:

$$\frac{(6.24)12 \frac{(2097)}{(2 \times 56)} + 2240(0.0425)}{0.89} = 1682 \text{ lb. per ton product}$$

Since, however, the heat generated by the 100 per cent indirect reduction process exceeds that required to supply the practical thermal requirements of the process, just enough direct reduction may be permitted to lower the heat generated to the exact amount which the process requires. To our previous basic equation, we shall add the limitation that the heat generated by the products of reaction with one mol of iron oxide must equal 670,000 B.t.u. The basic equations then become

$$H + (w) C + (a) O_2 + Fe_2O_3 = 2Fe + (b) CO + (d) CO_2 + (670,000 - 345,000)$$

$$H = +325,000$$

and the four auxiliary equations become:

$$\text{Carbon balance, } w = b + d$$

$$\text{Oxygen balance, } 2(a) + 3 = b + 2(d)$$

$$\text{Limiting CO:CO}_2 \text{ ratio, } b = 1.08(d)$$

$$\text{Thermal balance, } 53,000b + 175,000d = 670,000$$

Solution of these equations yields the following coefficients:  $w = 5.99$  mols C,  $a = 2.93$  mols  $O_2$ ,  $b = 3.11$  mols CO,  $d = 2.88$  mols  $CO_2$ , and the general equation becomes:



The calculation of the heats of reaction is

$$H + 5.99(O) + 2.93(O) + 1(345,000) = 2(O) + 3.11(53,000) + 2.88(175,000)$$

$$H + 345,000 = 670,000$$

$$670,000 - 345,000 = +325,000 \text{ B.t.u. per pound mol } Fe_2O_3$$

which fulfills the heat requirement of Mathesius' heat balance.

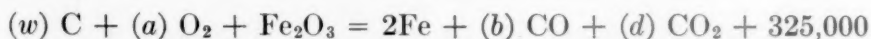
The theoretical coke rate of this practice would be

$$\frac{5.99(12) \frac{2097}{2 \times 56} + (0.0425)(2240)}{0.89} = 1620 \text{ lb. per ton product}$$

which would be a saving of 62 lb. coke per ton under that required by the 100 per cent indirect reduction process.

#### EFFECT OF BLAST HEAT ON BASIC REACTION OF REDUCTION

Analysis of the basic general equation, satisfying both the thermal and reduction functions of the carbon in the blast furnace,



shows that whatever may be the coefficients of the equation, they must be such that a constant amount of heat, 325,000 B.t.u. per mol of iron oxide consumed, is supplied. This is, however, a purely thermal requirement, which has no bearing whatsoever on the carbon needed for reduction. The heat may come from a source entirely external to the reaction. Any heat supplied externally lowers by an equal amount the thermal requirements that the equation must satisfy. Inspection of the equation also reveals that there is available in the gaseous products of the reaction, chemical latent heat in the form of carbon monoxide, which cannot be oxidized in the furnace because of the limiting ratio set by the equilibrium

relations discussed previously. If this carbon monoxide, can be burned to dioxide in an apparatus independent of the furnace and the heat so generated returned to the furnace, the thermal requirements of the equation will be lowered and the coefficients of the equation altered. This is the function of the blast heat—the recovery of that part of the latent chemical energy of the waste gases that cannot be recovered in the furnace because of the necessity for keeping the composition of the gases of a reducing nature.

The limiting equation of the blast-furnace process may then be calculated from the following assumptions:

1. Ratio of CO:CO<sub>2</sub> in gases = 1.08.

2. All the waste gases are burned in 80 per cent efficient heat exchangers, the heat from which is returned to the process.

The general equation of reduction is:



The thermal balance is:

$$53,000b + 175,000d + (0.8b)(175,000 - 53,000) = 670,000$$

Carbon balance,  $w = b + d$

Oxygen balance,  $2a + 3 = b + 2d$

Limiting gas ratio,  $b = 1.08d$

Solution of these equations yields the following coefficients:  $w = 4.12$  mols C,  $a = 1.55$  mols O<sub>2</sub>,  $b = 2.14$  mols CO,  $d = 1.98$  mols CO<sub>2</sub>, and the equation becomes:



That the thermal requirements are satisfied are shown by the thermal balance:

$$\begin{aligned} H + 4.12(\text{O}) + 1.55(\text{O}) + 1(345,000) &= 2(\text{O}) + 2.14(53,000) + \\ &1.98(175,000) + 2.14(0.8)(175,000 - 53,000) \\ H + 345,000 &= 670,000 \end{aligned}$$

Heat of reaction = +325,000 B.t.u. per pound mol Fe<sub>2</sub>O<sub>3</sub>, which satisfies the thermal requirement of the process.

The heat returned to the furnace by the blast in this case would be

$$(0.8)(2.14)(175,000 - 53,000) = 209,000 \text{ B.t.u.,}$$

which would require a blast temperature of about 3970° F.

The theoretical coke rate of such a practice would be

$$\frac{4.12(12) \frac{2097}{2 \times 56} + 0.0425(2240)}{0.89} = 1148 \text{ lb. per ton product,}$$



which is a reduction of 534 lb. from the theoretical coke rate of a 100 per cent indirect reduction process. Thus, the direct reduction, which was permitted thermally by the return to the process of 80 per cent of the available heat content of the gases, in the form of blast heat, has resulted in a decrease in the theoretical coke requirements of  $\frac{534}{1682} = 31.7$  per cent.

That this practice cannot be obtained in the blast furnace is apparent from the fact that the blast temperature required is in excess of the theoretical flame temperature of blast-furnace gas. The equation is of interest, however, in that it represents the limit of fuel economy in the furnace when the waste gases are of equilibrium composition and as much of the heat of combustion of the carbon in the exit gas is returned to the furnace as is possible to recover in modern heat exchangers.

To illustrate the effect on fuel economy of the direct reduction permitted by blast heats carried in present practice, the equations at equilibrium conditions for blast heats of 800° F. and 1600° F. are calculated below:

Basis of calculations:

1. Total heat supplied to reaction = 670,000 B.t.u.
2. Limiting ratio  $\text{CO}:\text{CO}_2 = 1.08$ .
3. A portion of the exit gas is burned in 80 per cent efficient stoves, the heat evolved being returned to the furnace by blast temperature of 800° F.

Heat content of preheated air per mol of  $\text{O}_2$  reacting with C at the tuyeres:

$$\frac{0.248(800 - 32)(29)}{0.21} = 26,300 \text{ B.t.u.}$$

General equation:



Thermal balance:

$$175,000d + 53,000b + (b)K(175,000 - 53,000) = 670,000$$

where  $K$  = per cent of heat of combustion of CO in exit gas returned to the reaction in the form of preheated air.

Heat of preheated air:

$$26,300a = (b)K(175,000 - 53,000)$$

Carbon balance,  $w = b + 2d$

Oxygen balance,  $2a + 3 = b + 2d$

Limiting  $\text{CO}:\text{CO}_2$  ratio,  $b = 1.08d$

Solution of these equations yields:  $w = 5.41$  mols C,  $a = 2.505$  mols  $\text{O}_2$ ,  $b = 2.81$  mols CO,  $d = 2.60$  mols  $\text{CO}_2$ ,  $K = 19.2$  per cent.

Substituting these in the general equation:



Heat supplied to process:

Heat of oxidation C to  $\text{CO}_2$ :  $2.60 \times 175,000 = 455,000$  B.t.u.

Heat of oxidation C to CO:  $2.81 \times 53,000 = 149,000$  B.t.u.

19.2 per cent heat of combustion exit gas:

$2.81(0.192)(175,000 - 53,000)$  to be supplied by 2.505 pound mols air with a heat content of 26,300 B.t.u. per pound mol

$$= 66,000 \text{ B.t.u.}$$

Total heat supplied

$$= 670,000 \text{ B.t.u.}$$

which satisfies the thermal requirements.

Gas burned in 80 per cent efficient stoves =  $\frac{0.192}{0.80} \times 100 = 24.0$  per cent.

$$\text{Theoretical coke rate} = \frac{5.41(12)\frac{2097}{2 \times 56} + 0.0425(2240)}{0.89} = 1472 \text{ lb.}$$

In a similar manner, calculations for a blast temperature of  $1600^\circ \text{F.}$  give the following results:

General equation:



Heat of combustion of exit gas utilized to preheat blast = 37.1 per cent.

Exit gas burned in 80 per cent efficient stoves:

$$\frac{0.371}{0.80} = 46.4 \text{ per cent}$$

Theoretical coke rate: 1385 lb. per ton pig.

The results of these calculations, with the exit gases in all instances at equilibrium conditions, are summarized in Table 4. From the table, the following conclusions may be drawn:

1. When all the carbon is burned at the tuyeres, more heat is generated than is required by the process. Any heat returned to the process in the form of blast heat does not reduce the carbon requirement, since the carbon required is set by the reduction function and not by the thermal requirements.

2. As the amount of direct reduction increases, the carbon requirement for reduction purposes decreases.

TABLE 4.—*Summary of Calculations*  
EXIT GASES AT EQUILIBRIUM

Reduction	Fuel Carbon Burned at Tuyeres, Per Cent	Total Heat of Reaction	Total Heat Necessary to Process	CO: CO <sub>2</sub> Ratio (Fuel C Basis)	Exit CO Burned in Stoves, Per Cent	Blast Temperature, Deg. F.	Coke Rate, Lb. per Ton Pig
1. 100 per cent indirect..	100.0	697,000	670,000	1.08	0		1,682
2. Partial direct.....	97.7	670,000	670,000	1.08	0		1,620
3. Partial direct.....	92.5	604,000	670,000	1.08	24.0	800	1,472
4. Partial direct.....	87.6	553,000	670,000	1.08	46.4	1600	1,385
5. Partial direct.....	75.3	461,000	670,000	1.08	100	3970	1,148

3. As the percentage of carbon burned at the tuyeres decreases, the process encounters a thermal deficiency, which increases inversely to the carbon burned at the tuyeres.

4. Within certain limits, this thermal deficiency may be overcome by the return to the process of the heat of combustion available in the carbon monoxide of the top gases.

5. The return to the furnace of the heat of combustion of the carbon monoxide of the top gases increases the efficiency of the carbon.

#### NONEQUILIBRIUM CONDITIONS

The foregoing discussion has been based on the condition that the furnace gases attain equilibrium. Needless to say, the attainment of equilibrium, under conditions prevailing in the blast furnace, is impossible. Various methods of increasing the concentration of carbon dioxide in the top gases, such as Avery's<sup>10</sup> proposed high-pressure operation, have been suggested. The extent to which such methods would help, however, awaits determination.

In order that the present study may be applicable to conditions under which modern furnaces operate, Tables 5, 6, 7 and 8 have been calculated. These tables show the effect of varying amounts of direct reduction on the carbon requirements of the furnace under all top gas compositions encountered in normal furnace practice. Various compositions of the top gas are assumed under the conditions given. The carbon required for reduction and the heat effect of the process are calculated. The heat effect of the process per pound of iron produced is then compared with the 6127 B.t.u., which is shown, by Mathesius' heat balance, to be required by the furnace for the industrial production of 1 lb. Fe.

To illustrate this method, the following calculations are shown for Table 5, where 100 per cent of the carbon is burned at the tuyeres and the case where the ratio of the gases from the fuel carbon is 2.0. This is the third horizontal line of the table.

TABLE 5.—100 Per Cent Fuel Carbon Burned at Tuyeres  
No DIRECT REDUCTION

(1) Ratio CO:CO <sub>2</sub> in Gases from Fuel C	(2) Ratio CO:CO <sub>2</sub> in Top Gases (In- cluding Limestone Calcina- tion)	(3) CO <sub>2</sub> in Top Gas, Mols per Mol C	(4) Mols Fe Reduced per Mol C		(7) Pounds C per Pound Fe	(8) Pounds C to CO <sub>2</sub>	(9) Pounds C to CO	(10) Heats of Reaction		(12) Total Heat	(13) Excess B.t.u. (6127 Basis)	(14) C Burned at Tuyeres per Pound Fe	(15) Pounds at Blast per Pound Fe	(16) B.t.u. Con- tent of Blast per Deg. F.	(17) Heat of Blast Necessary to Make Up Deficit, Deg. F.
			By Carbon	Total				C to CO <sub>2</sub>	C to CO						
4.00	3.67	0.200	None	0.133	1.612	0.322	1.290	4.685	5.680	10,365	4.238	1.612	No blast preheat required		
3.00	2.74	0.250	None	0.167	1.284	0.322	0.962	4.685	4.235	8,920	2,793	1.284	No blast preheat required		
2.00	1.83	0.333	None	0.222	0.964	0.322	0.642	4.685	2.825	7,510	1,383	0.964	No blast preheat required		
1.50	1.37	0.400	None	0.267	0.803	0.322	0.481	4.685	2.117	6,802	675	0.803	No blast preheat required		
1.25	1.14	0.444	None	0.296	0.724	0.322	0.402	4.685	1.769	6,454	327	0.724	No blast preheat required		
1.00	0.92	0.500	None	0.333	0.644	0.322	0.322	4.685	1.418	6,103	—	0.644	No blast preheat required	3.73	26

TABLE 6.—90 Per Cent Fuel Carbon Burned at Tuyeres  
10 PER CENT CARBON USED FOR DIRECT REDUCTION

(1) Ratio CO:CO <sub>2</sub> in Gases from Fuel C	(2) Ratio CO:CO <sub>2</sub> in Top Gases (In- cluding Limestone Calcina- tion)	(3) CO <sub>2</sub> in Top Gas, Mols per Mol C	(4) Mols Fe Reduced per Mol C		(7) Pounds C per Pound Fe	(8) Pounds C to CO <sub>2</sub>	(9) Pounds C to CO	(10) Heats of Reaction		(12) Total Heat	(13) Excess B.t.u. (6127 Basis)	(14) C Burned at Tuyeres per Pound Fe	(15) Pounds at Blast per Pound Fe	(16) B.t.u. Con- tent of Blast per Deg. F.	(17) Heat of Blast Necessary to Make Up Deficit, Deg. F.
			By Carbon	Total				C to CO <sub>2</sub>	C to CO						
4.00	3.51	0.200	0.067	0.133	1.070	0.214	0.856	3.113	3.770	6,883	756	0.963	5.57	1.380	None required
3.00	2.65	0.250	0.067	0.167	0.920	0.230	0.690	3.348	3.040	6,388	261	0.828	4.78	1.187	None required
2.00	1.76	0.333	0.067	0.222	0.741	0.247	0.494	3.594	2.175	5,769	—	0.667	3.86	0.957	374
1.50	1.34	0.400	0.067	0.267	0.644	0.258	0.386	3.753	1.697	5,450	—	0.580	3.35	0.831	815
1.25	1.13	0.444	0.067	0.296	0.591	0.262	0.329	3.815	1.449	5,264	—	0.532	3.08	0.764	1,129
1.00	0.90	0.500	0.067	0.333	0.536	0.268	0.268	3.900	1.180	5,080	—1,047	0.482	2.79	0.692	1,512

TABLE 7.—85 Per Cent Fuel Carbon Burned at Tuyeres  
15 PER CENT CARBON USED FOR DIRECT REDUCTION

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)
Ratio CO:CO <sub>2</sub> in Gases from Fuel C	Ratio CO:CO <sub>2</sub> in Top Gases (In- cluding Limestone Calcina- tion)	CO <sub>2</sub> in Top Gas, Mols per Mol C	Mols Fe Reduced per Mol C		Pounds C per Pound Fe	Pounds C to CO <sub>2</sub>	Pounds C to CO	Heats of Reaction		Total Heat	Excess B.t.u. (6127 Basis)	C Burned at Tuyeres per Pound Fe	Pounds Blast per Pound Fe	B.t.u. Con- tent of Blast per Deg. F.	Heat of Blast Necessary to Make Up Deficit, Deg. F.	
			By Carbon	By CO				C to CO <sub>2</sub>	C to CO							
4.00	3.44	0.200	0.100	0.133	0.233	0.920	0.184	0.736	2,679	3,240	5,919	208	0.782	4.52	1,121	186
3.00	2.60	0.250	0.100	0.167	0.267	0.803	0.201	0.602	2,926	2,650	5,576	551	0.883	3.96	0.979	563
2.00	1.76	0.333	0.100	0.222	0.322	0.666	0.222	0.444	3,230	1,954	5,184	943	0.566	3.28	0.812	1,161
1.50	1.33	0.400	0.100	0.267	0.367	0.584	0.234	0.350	3,406	1,540	4,946	1,181	0.496	2.87	0.714	1,653
1.25	1.11	0.444	0.100	0.296	0.396	0.542	0.241	0.301	3,508	1,325	4,833	1,294	0.461	2.67	0.664	1,950
1.00	0.89	0.500	0.100	0.333	0.433	0.496	0.248	0.248	3,610	1,092	4,702	1,425	0.422	2.44	0.607	2,346

TABLE 8.—80 Per Cent Fuel Carbon Burned at Tuyeres  
20 PER CENT CARBON USED FOR DIRECT REDUCTION

(1)	(2)	(3)	(4)		(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	
Ratio CO:CO <sub>2</sub> in Gases from Fuel C	Ratio CO:CO <sub>2</sub> in Top Gases (In- cluding Limestone Calcina- tion)	CO <sub>2</sub> in Top Gas, Mols per Mol C	Mols Fe Reduced per Mol C		By Carbon	By CO	Total	Pounds C per Pound Fe	Pounds C to CO <sub>2</sub>	Pounds C to CO	Heats of Reaction		Total Heat	Excess B.t.u. (6127 Basis)	C Burned at Tuyeres per Pound Fe	Pounds Blast per Pound Fe	B.t.u. Con- tent of Blast per Deg. F.	Heat of Blast Necessary to Make Up Deficit, Deg. F.
			C to CO <sub>2</sub>	C to CO														
4.00	3.36	0.200	0.133	0.133	0.266	0.803	0.161	0.642	2,342	2,824	5,166	—	961	0.642	3.71	0.920	1,045	
3.00	2.56	0.250	0.133	0.167	0.300	0.714	0.179	0.535	2,603	2,353	4,956	—	1,171	0.571	3.30	0.818	1,431	
2.00	1.73	0.333	0.133	0.223	0.356	0.602	0.201	0.401	2,922	1,765	4,687	—	1,440	0.482	2.79	0.691	2,085	
1.50	1.31	0.400	0.133	0.267	0.400	0.536	0.215	0.321	3,127	1,413	4,540	—	1,587	0.429	2.48	0.615	2,580	
1.25	1.10	0.444	0.133	0.296	0.429	0.498	0.221	0.277	3,215	1,218	4,433	—	1,694	0.398	2.30	0.571	2,965	
1.00	0.88	0.500	0.133	0.333	0.467	0.458	0.229	0.229	3,330	1,008	4,338	—	1,789	0.366	2.12	0.525	3,405	



Column 1 is the  $\text{CO}:\text{CO}_2$  ratio in the top gases from the oxidation of the fuel carbon. In the present calculation, this is assumed to be 2.0.

Column 2 shows the top gas composition that would be obtained under this assumption by an analysis of the top gases. Since this includes the carbon dioxide resulting from the limestone calcination, the  $\text{CO}:\text{CO}_2$  ratio must be lower than the ratio of the  $\text{CO}:\text{CO}_2$  of the gases from the fuel carbon alone. As this calculation is dependent on the amount of carbon required per pound of iron, it cannot be made until the carbon requirement is determined in a later step. The method of calculation is shown in step 9, but the result is inserted in column 2 to show the top gas composition that would be determined by an actual gas analysis.

Column 3 represents the mols of carbon dioxide in the top gas per mol of fuel carbon charged. One mol of carbon produces one mol of carbon gases. The assumption in column No. 1 is that the  $\text{CO}:\text{CO}_2$  ratio is 2.0. The  $\text{CO}_2$  in the gases will therefore be:

$$\frac{1}{2 + 1} = \frac{1}{3} = 0.333$$

Columns 4, 5 and 6 show the iron reduced under these conditions. Column 4 is the iron reduced by solid carbon. Since the assumption in this instance is that all the carbon is burned at the tuyeres, no iron will be reduced by carbon. Column 5 shows the iron reduced by carbon monoxide per mol of carbon burned. This is calculated as follows:

The CO produced by the carbon at the tuyeres ( $\text{C} + \frac{1}{2}\text{O}_2 = \text{CO}$ ) reacts with  $\text{Fe}_2\text{O}_3$  as follows:



In this reaction,  $\frac{2}{3}$  mol Fe is reduced in the formation of one mol  $\text{CO}_2$ . From column 3, the top gas contains 0.333 mols  $\text{CO}_2$ , therefore the iron reduced per mol of carbon is:

$$\frac{2}{3} \times 0.333 = 0.222 \text{ mols Fe}$$

Column 6 shows the total mols Fe reduced. In this case, since no iron is reduced by solid carbon, column 6 is numerically equal to column 5.

Column 7 shows the pounds of carbon required per pound of iron reduced. This is equal to:

$$\frac{\text{Molecular weight C}}{\text{Mols Fe reduced} \times \text{molecular weight Fe}} = \frac{12}{0.222 \times 56} = 0.964 \text{ lb. C per pound Fe.}$$

Columns 8 and 9 show the extent of oxidation of the carbon. The pounds of carbon burned to  $\text{CO}_2$ , as shown by column 8, is calculated:

$$0.964 \text{ lb. C} \times 0.333(\text{per cent } \text{CO}_2) = 0.322 \text{ lb. C to } \text{CO}_2$$

The pounds of carbon burned to CO, shown in column 9, is obtained by subtracting the C burned to CO<sub>2</sub> from the total carbon:

$$0.964 - 0.322 = 0.642 \text{ lb. C to CO}$$

The final gas composition, as shown in column 2, may now be calculated:

Assume 0.25 lb. limestone per lb. Fe.

Molecular weight CaCO<sub>3</sub> = 100.

Pounds C in CO<sub>2</sub> of limestone:

$$\frac{0.25}{100} \times 12 = 0.030$$

Total C forming CO<sub>2</sub> in top gas:

$$\text{Fuel C to CO}_2 + \text{C in limestone} = 0.322 + 0.030 = 0.352 \text{ lb.}$$

$$\text{Final ratio CO:CO}_2 \text{ in top gas} = \frac{\text{Pounds C to CO}}{\text{Total C to CO}_2} = \frac{0.642}{0.352} = 1.83$$

Columns 10, 11 and 12 show the heat of reaction from the formation of the CO and CO<sub>2</sub>.

The heat of reaction of the C to CO<sub>2</sub> is shown in column 10. This is calculated from heat of combustion data as follows:

$$0.322(\text{lb. C to CO}_2) \times 14,550 = 4685 \text{ B.t.u. per lb. Fe}$$

Column 11 gives the heat produced by the CO:

$$0.642(\text{lb. C to CO}) \times 4400 = 2825 \text{ B.t.u. per lb. Fe}$$

Column 12 shows the total heat effect, which is the sum of columns 10 and 11:

$$4685 + 2825 = 7510 \text{ B.t.u. per lb. Fe}$$

Mathesius' heat balance shows that 6127 B.t.u. are required by the blast furnace for the industrial production of a pound of Fe.

Column 13 compares the heat produced in the furnace with that required by the furnace. The present practice produces 7510 B.t.u. per lb. Fe. Since this is in excess of the 6127, which Mathesius shows to be required, a surplus of heat above that required, equal to

$$7510 - 6127 = 1383 \text{ B.t.u. per lb. Fe}$$

is produced. Since the process has already met the thermal requirements set by Mathesius, it is apparent that no blast heat is needed, and that because of the limitations set by the reduction process, more heat is produced in the furnace than is needed.

In Tables 6, 7 and 8 are shown the results of burning less than 100 per cent of the carbon at the tuyeres. As a sample of these calculations, the

example shown in Table 7, where only 85 per cent of the carbon is burned at the tuyeres and the ratio of  $\text{CO}:\text{CO}_2$  in the gases from the fuel carbon is 2.00, as in the previous example, will be calculated. This is the third line in Table 7.

Columns 1, 2 and 3 are derived in the same manner as the same columns in the previous calculations. Column 4, however, denotes the iron from direct reduction. The reaction in this case is



by which  $\frac{2}{3}$  mol Fe is reduced by one mol of carbon. Under the assumption that 15 per cent of the carbon reacts directly, the iron reduced directly per mol of fuel carbon charged will be:

$$\frac{2}{3} \times 0.15 = 0.10 \text{ mols}$$

Column 5 is calculated in the same way as column 5 in the previous example. The mols of Fe formed from the reaction of CO is:

$$\frac{2}{3} \times 0.333(\text{mols CO}_2) = 0.222 \text{ mols Fe}$$

The total iron reduced, as shown by column 6, will be the sum of the two previous columns:

$$0.100(\text{from direct}) + 0.222(\text{from indirect reduction}) = 0.322 \text{ mols Fe per mol C}$$

Column 7 is calculated exactly as before and is equal to

$$\frac{\text{Molecular weight C}}{\text{Mols Fe produced} \times \text{molecular weight Fe}} = \frac{12}{0.322 \times 56} = 0.666 \text{ lb. C per pound Fe reduced.}$$

Column 8 again shows the pounds of C burned to  $\text{CO}_2$  in the top gases per pound Fe:

$$0.666(\text{lb. C per lb. Fe}) \times 0.333(\text{per cent CO}_2 \text{ in top gas}) = 0.222$$

Column 9 gives the pounds C burned to CO and is obtained by deducting the C to  $\text{CO}_2$  from the total C:

$$0.666 - 0.222 = 0.444$$

From these data, the final ratio  $\text{CO}:\text{CO}_2$ , including the  $\text{CO}_2$  from limestone calcination, is obtained. In this case the ratio is

$$\frac{\text{Pounds C to CO}}{\text{Pounds C to CO from fuel} + \text{pounds C in limestone}} = \frac{0.444}{0.222 + 0.030} = \frac{0.444}{0.252} = 1.76$$

Columns 10, 11 and 12 are calculated exactly as before.

Column 10, heat of formation of  $\text{CO}_2$ ,  $0.222 \times 14,550 = 3230$  B.t.u.

Column 11, heat of formation of  $\text{CO}$ ,  $0.444 \times 4400 = 1954$  B.t.u.

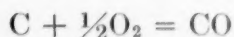
Column 12, total heat produced in furnace,  $3230 + 1954 = 5184$  B.t.u.

The difference between the heat produced and that required, as shown in column 13, is obtained by subtracting 6127 B.t.u. from 5184 B.t.u. or,  $5184 - 6127 = -943$  B.t.u., which shows that under the assumed conditions, 943 B.t.u. less than the required heat per pound of iron are generated in the furnace. How this heat deficiency may be made up by blast heat has been shown in a previous section. The remaining columns in the table show the steps in calculating the blast temperature necessary to balance the heat deficiency.

Column 14 represents the pounds C burned at the tuyeres per pound Fe produced:

$$0.666 \times 0.85(85 \text{ per cent C burned at tuyeres}) = 0.566 \text{ lb.}$$

The pounds of air blown per pound iron, as shown in column 15, is:



Air = 23 per cent oxygen by weight. Air blown per pound Fe =

$$0.566 \times \frac{16}{12} \times \frac{1.00}{0.23} = 3.28 \text{ lb. air per pound Fe}$$

Column 16 represents the heat content of the air per degree Fahrenheit:

Mean specific heat of air = 0.248 B.t.u. per lb. per deg. F.

$$3.28 \times 0.248 = 0.812 \text{ B.t.u. per lb. air per deg. F.}$$

Column 17 shows the blast temperature required to supply the heat deficiency:

$$\frac{\text{B.t.u. deficit}}{\text{B.t.u. content of air per deg. F}} = \frac{943}{0.812} = 1161^\circ \text{ F.}$$

In every instance the carbon necessary for carburizing the iron has not been considered in the calculations. In using the tables to calculate estimated coke rates, it is necessary to increase the coke rate by the amount of coke required to carburize the iron.

The data of the tables have been plotted on Figs. 2, 3 and 4. In all these curves, the abscissas represent actual ratio of  $\text{CO}:\text{CO}_2$  in the top gas. The top line on Fig. 2 represents the carbon required when burning 100 per cent carbon at the tuyeres, as shown in column 7 of Table 5. The line immediately below the carbon required represents the heat generated by the 100 per cent indirect reduction process, as shown in column 12, Table 5. The heavy horizontal line represents 6127 B.t.u., which has been shown by Mathesius to be required for the production of one pound of iron. It is apparent from these curves that the heat

generated by the carbon required for reduction purposes in the 100 per cent indirect reduction process under all possible compositions of top gas exceeds that required by the furnace. Under these conditions, no advantage may be taken of the waste heat in the gases, since no more heat is required by the process. As Austin has shown, the carbon requirement of the process is set by the reducing rather than by the thermal function.

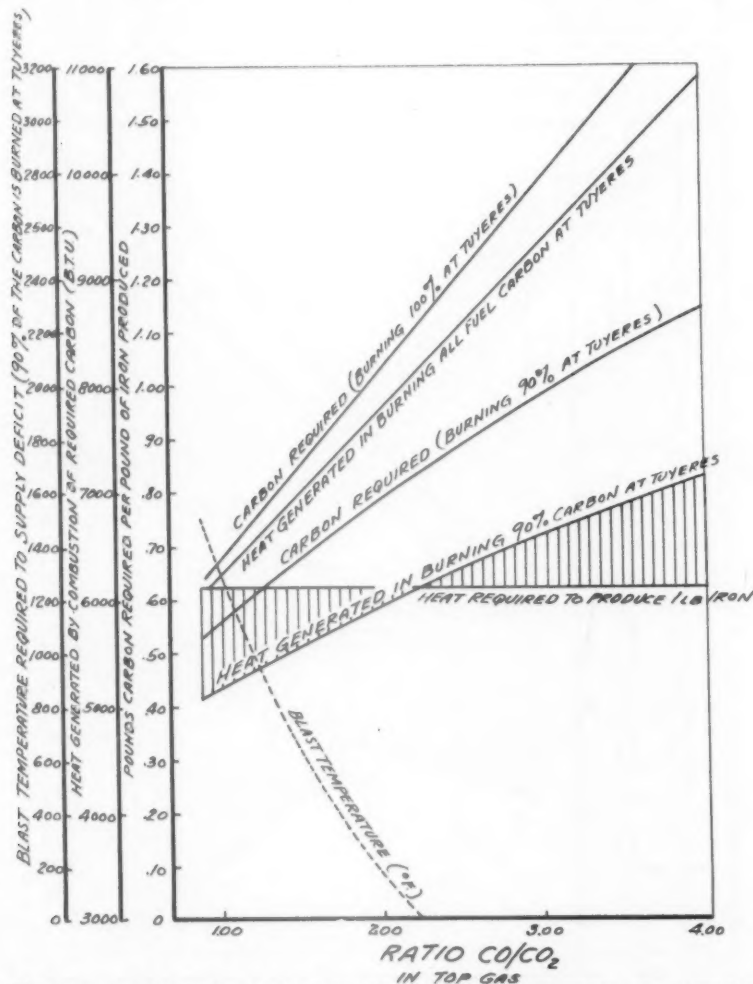


FIG. 2.—EFFECT OF VARYING AMOUNTS OF DIRECT REDUCTION ON CARBON REQUIREMENTS.

The third curve from the top on this figure represents the carbon required by a process where only 90 per cent of the carbon is burned at the tuyeres. This line shows that at all gas compositions the carbon requirement of this process is less than that of the 100 per cent indirect reduction process. The fourth curve from the top portrays the heat production of the 90 per cent indirect reduction process. This line crosses the horizontal 6127 B.t.u. line when the  $\text{CO}:\text{CO}_2$  ratio reaches 2.25. When the ratio is higher than 2.25 there is still excess heat generated



by the reaction. As the carbon monoxide in the top gas decreases below a ratio of 2.25, the process encounters a heat deficiency and would stop if it were not possible to supply additional heat. This heat is supplied in the form of blast heat, without, however, affecting the ore-reduction carbon requirement of the process. The blast temperature required to

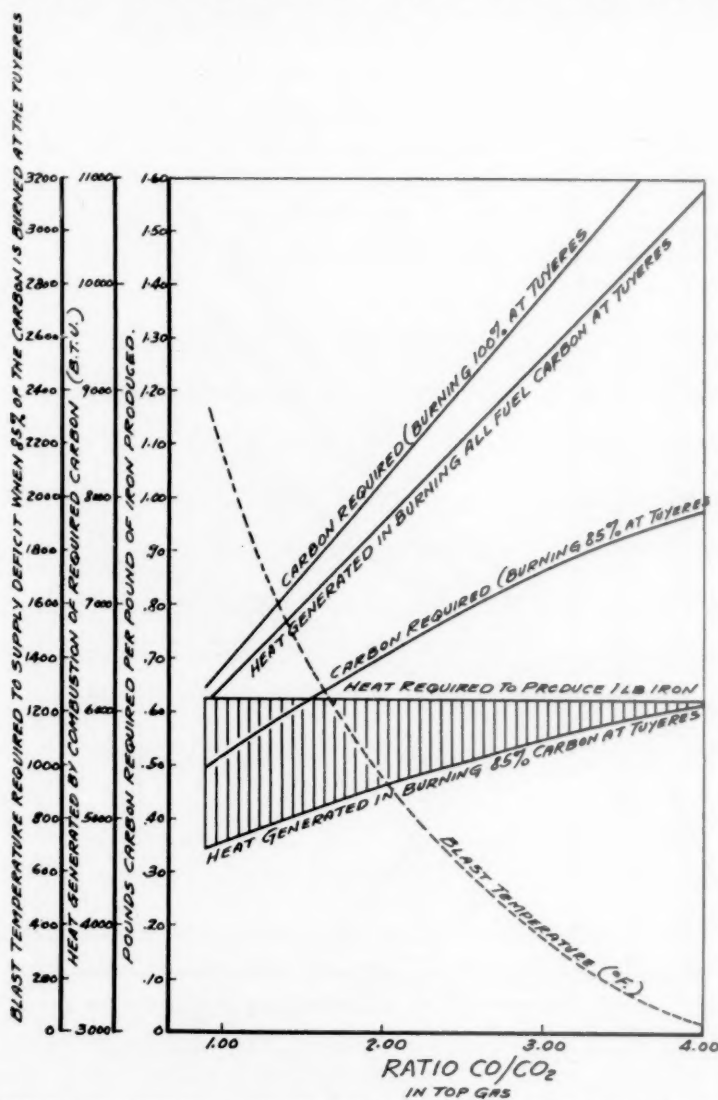


FIG. 3.—EFFECT OF VARYING AMOUNTS OF DIRECT REDUCTION ON CARBON REQUIREMENTS.

supply the heat deficiency is shown by the broken line at the lower left-hand corner of the diagram.

Fig. 3 is similar to Fig. 2, except that it portrays the carbon and thermal relations when only 85 per cent of the carbon is burned at the tuyeres. The curves of the 100 per cent indirect reduction process are shown for comparison. The carbon requirement is lower than in either

of the previous cases and the process produces a heat deficiency with all gas compositions below a  $\text{CO}:\text{CO}_2$  ratio of 4.0. The higher blast temperatures required to balance the heat deficiency are shown by the dotted line. With a gas ratio of 2.0  $\text{CO}:\text{CO}_2$ , this curve shows that when 85 per

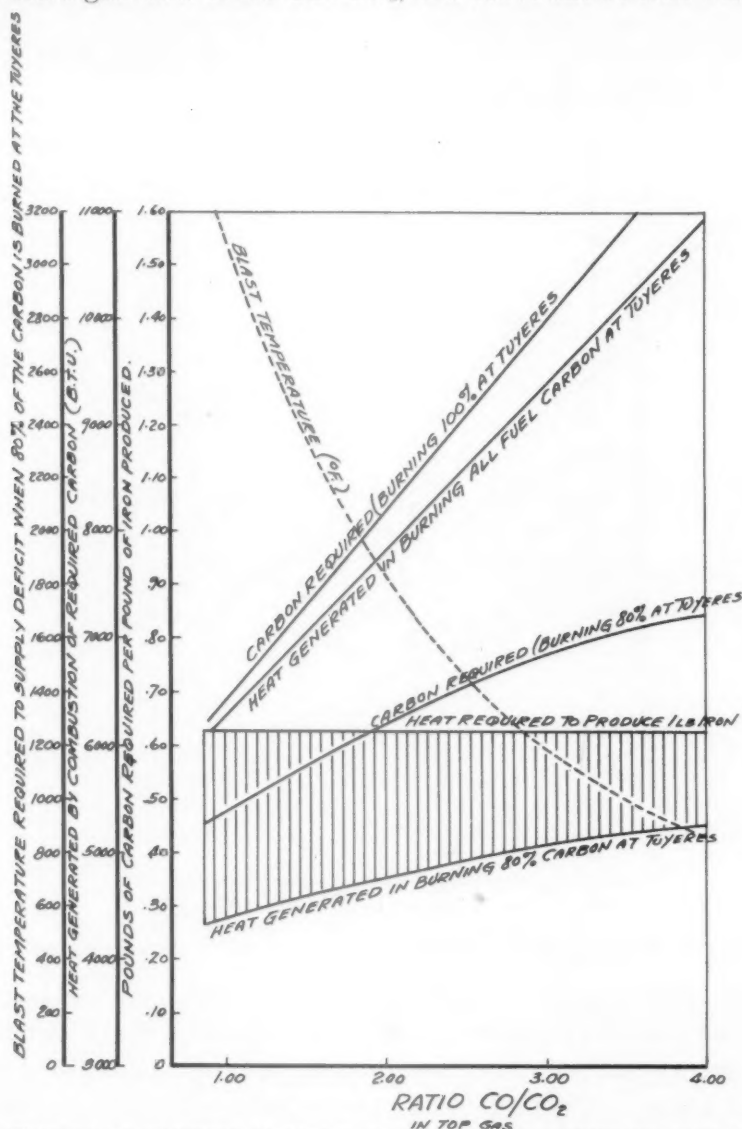


FIG. 4.—EFFECT OF VARYING AMOUNTS OF DIRECT REDUCTION ON CARBON REQUIREMENTS.

cent of the C is burned at the tuyeres, 0.70 lb. C is required per pound Fe, a heat deficiency of 877 B.t.u. is encountered and a blast temperature of  $950^\circ$  is required.

Fig. 4 is similar to the other two except that it shows the results of a practice where only 80 per cent of the carbon is burned at the tuyeres. The carbon required has decreased still more, the heat deficiency is greater, and higher blast temperatures are required. In fact, such high

blast temperatures are needed that the limit has been passed where direct reduction may be carried out in present practice. The curve shows that with a gas ratio of 2.00, a blast temperature of 1850° F. is required. Since, in the present state of blast-furnace development, such temperatures have been neither used nor developed, it would appear that practicalities set a limit to the carbon beneficial in direct reduction of about 15 to 20 per cent of the total.

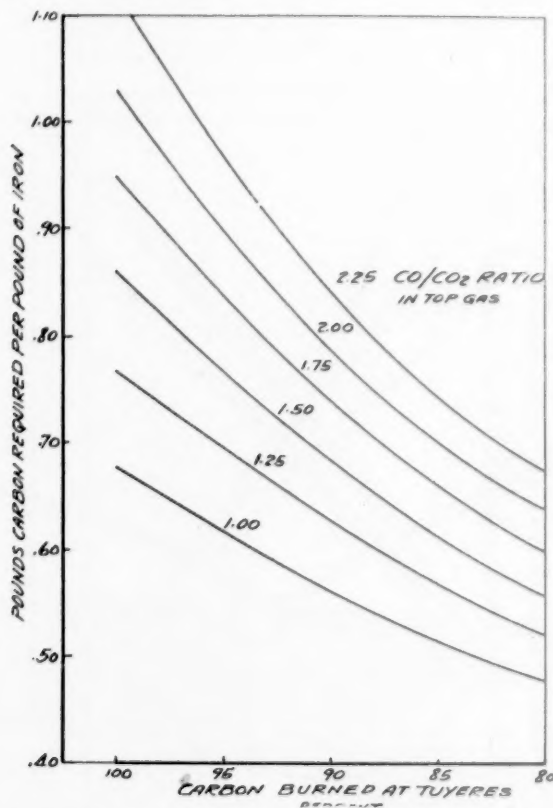


FIG. 5.—EFFECT OF INCREASING DIRECT REDUCTION WITH CONSTANT GAS COMPOSITION.

Certain other aspects of these data have been condensed into Fig. 5, which shows the effect of increasing direct reduction under constant gas composition conditions. Each line represents a constant ratio of CO:CO<sub>2</sub> in the top gases. Study of these curves demonstrates that less carbon is required as the CO<sub>2</sub> increases in the top gas and that less carbon is likewise required as the direct reduction increases under any given gas composition condition.

Fig. 6 shows the percentage of the available heat of the carbon utilized in the furnace under varying conditions of direct reduction and gas composition. It is apparent that the thermal efficiency is increased both by greater indirect reduction, as expressed by the carbon dioxide content of the gas, and also by greater direct reduction, as indicated by a decrease in the carbon burned at the tuyeres. The increase in the

thermal efficiency as the direct reduction increases is a result of crediting the process with the blast heat that is needed to balance the thermal requirements under direct reducing conditions.

The clearest conception of the influence of direct reduction in decreasing carbon consumption in the furnace may be had from a comparison of the carbon requirements of the process under the condition that the  $\text{CO}:\text{CO}_2$  ratio is 2.0, which approximates normal American practice. Such a comparison is made in Table 9.

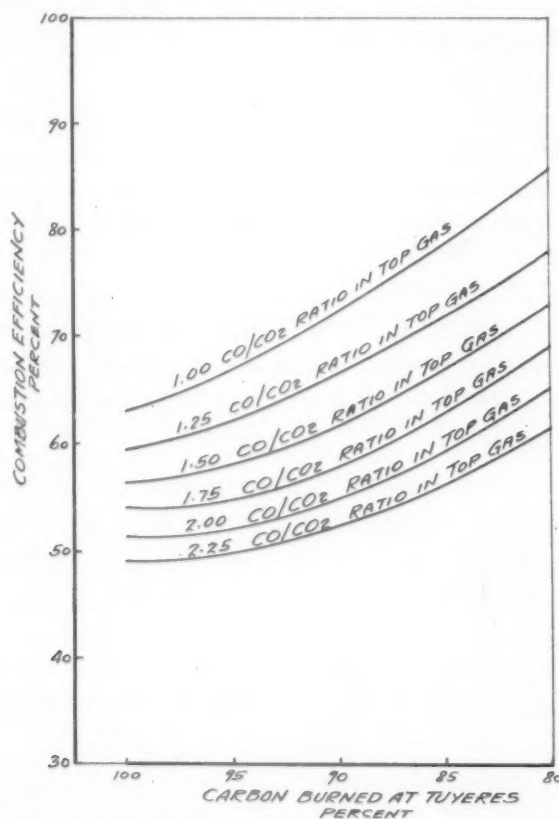


FIG. 6.—PERCENTAGE OF AVAILABLE HEAT OF CARBON UTILIZED IN FURNACE UNDER VARYING CONDITIONS OF DIRECT REDUCTION AND GAS COMPOSITION.

Such a table may be established from the curves in Figs. 2, 3 and 4 for any ratio of gas composition from 1.0 to 4.0. In every case the carbon requirement and coke rate of the process will decrease as less carbon is burned by the blast at the tuyeres. From this evidence, the conclusion must be drawn that furnace efficiency is promoted by direct reduction.

#### CONCLUSIONS

This study has attempted to analyze the thermochemical functions of the blast-furnace process for the particular purpose of determining the effect on furnace efficiency of the so-called solution-loss reactions. In our opinion this analysis proves that:

TABLE 9.—*Comparison of Carbon Requirements*

Indirect Reduction, Per Cent	Carbon Requirement, Lb. C per Lb. Fe	Blast Temperature Required to Supply Heat Deficit, Deg. F.	Coke Rate, Lb. per Ton Product
100	1.02		2,520
90	0.79	190	1,969
85	0.70	950	1,758
80	0.64	1850	1,612

1. The greatest efficiency of the blast furnace may not be attained when the reduction is performed entirely by carbon monoxide as demanded by Gruner's definition of the ideally perfect working of the blast furnace.

2. The so-called solution-loss reactions, which should more properly be termed direct-reduction reactions, promote furnace efficiency.

3. In modern blast-furnace practice, the carbon consumption of the process is determined primarily by the carbon needed for reduction purposes; any thermal deficiency created by the reduction process being balanced in practice by the use of blast heat.

4. The function of the blast heat is to balance the thermal deficiency caused by direct reduction. Since direct reduction greatly promotes reduction efficiency, the application of blast heat reduces the thermal requirements to a greater degree than would be indicated by the added heat content of the blast.

#### ACKNOWLEDGMENTS

The writer wishes to acknowledge the generous assistance of his colleagues at the South Works of the Carnegie-Illinois Steel Corporation, particularly Messrs. G. E. Steudel, J. M. Stapleton, C. G. Hogberg and H. E. Kaufman.

He also wishes to thank Messrs. H. A. Strain, W. E. Brewster and S. F. Urban, whose suggestions and kindly criticism have been most helpful.

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## DISCUSSION

(H. A. Strain presiding)

H. W. JOHNSON,\* East Chicago, Ind.—Mr. Martin is to be congratulated upon his novel presentation of this problem and the tremendous amount of work he has done. There are some phases of the discussion I question, particularly the conclusion that increasing solution loss results in higher efficiency. It is well known to the operator that when the furnace suddenly travels at an excessive rate it generally goes cold. If the wind blown is constant, the pounds of coke burned at the tuyeres must be constant. The excessive rate of travel is due to the fact that more coke is consumed in the stack in solution-loss reactions, and the furnace goes cold. It is true that frequently efficient operation is accompanied by high solution loss, but we cannot conclude therefore that all increases in solution loss cause increased furnace efficiency.

I question also the conclusion that the limiting factor in furnace efficiency is the reducing power of the gas and not the temperature of the hearth. Mr. Martin comes to this conclusion from a series of calculations, one of which is based on the assumption that the ratio of CO to CO<sub>2</sub> cannot exceed 1:1. Richards<sup>11</sup> makes the same assumption when he says: "The real reaction of reduction by CO gas is therefore more nearly represented by



and arrives at a similar conclusion. Howland<sup>12</sup> attacks the problem by a similar method and precedes his calculations with the statement: "I shall assume for the purpose of our discussion that the reduction of the Fe<sub>2</sub>O<sub>3</sub> by either CO or C takes place under such conditions as to produce a ratio of 1 to 1 in the resulting gas." (CO to CO<sub>2</sub>.) Walther Mathesius<sup>13</sup> objects to Richards' way of writing the equation because: "There are three molecules of CO introduced into the . . . equation which are by no means essential for the carrying on of the reaction, in which they are taking no part."

The accuracy of this assumption is extremely important, as it is the determining factor in all such calculations. The question is: What is the leanest gas that it is possible to produce in a blast furnace? Matsubara<sup>14</sup> has studied the equilibrium of iron, carbon and oxygen and his data indicate clearly that gas containing only a few per cent of CO will reduce hematite to magnetite at certain temperatures. From these data we see that the top gas issuing from a blast furnace is still strongly reducing to hematite and so we cannot state that the limiting factor is the deficiency in the reducing power of the gas. The fact remains that we have not been able to produce top gas approaching the limits set by Matsubara. But the responsibility for failure is ours. If we were more adventurous and departed from the conventional dimensions, we might approach it.

L. F. SATTELE,† McKeesport, Pa.—From a theoretical point of view this study has shown definitely that solution loss within certain limits is of assistance in increasing

\* Superintendent Blast Furnaces, Inland Steel Co.

<sup>11</sup> J. W. Richards: *Metallurgical Calculations*, 278. New York, 1918. McGraw-Hill Book Co.

<sup>12</sup> H. P. Howland: *Calculations with Reference to the Use of Carbon in Modern American Blast Furnaces*. *Trans. A.I.M.E.* (1916) **56**, 342.

<sup>13</sup> W. Mathesius: *Chemical Reactions of Iron Smelting*. *Amer. Iron and Steel Inst.* (1917).

<sup>14</sup> A. Matsubara: *Chemical Equilibrium between Iron, Carbon and Oxygen*. *Trans. A.I.M.E.* (1922) **67**, 3.

† Superintendent Blast Furnaces, National Works, National Tube Co.

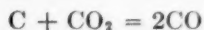
the efficiency of the blast furnace. However, in a process as complex as the blast furnace, where many practical considerations enter into the problem, it is difficult even to predict how close the ideal operation as set forth by the author can be approached. These practical considerations, which include quality of coke, nature of the ore, availability of high blast temperature, furnace lines and operating rate, will determine to a large extent the efficiency of a particular furnace.

The paper provides the answer to the successful utilization of high blast temperatures—that is, over 1400°F. I believe the successful utilization of high blast temperatures under normal operating conditions is the direct result of the necessity for supplying heat to the hearth to overcome the deficiency of heat resulting from a certain amount of direct reduction or solution loss. It is evident, therefore, that the two problems are related; namely, the processes that contribute to the greatest furnace efficiency and the economical utilization of high blast heats are related.

Some furnaces operate very efficiently on 100 per cent Mesabi ores, coke from 100 per cent high-volatile coal with blast heats averaging between 1100° and 1300°F. The Co-CO<sub>2</sub> ratio in the top gases of these furnaces was under 1.60 and the operating conditions were contributing to low solution loss. An even more efficient operation would no doubt have been obtained on these same furnaces with solution loss occurring within the limits proposed in this study provided the heat deficiency in the hearth could be overcome with blast heats in the range from 1600° to 1800°F. with a smoothly operating furnace. In my opinion, this is the answer from a theoretical standpoint to the problem of efficient furnace operation with reduction processes contributing to solution losses within the limits set forth in the study.

W. E. BREWSTER,\* South Chicago, Ill.—Mr. Martin's argument adds theoretical backing to the practical observations by Howland (ref. 12) and Brewster.<sup>15</sup> These authors give results of actual practice that indicate *insufficient* carbon available for the reduction of Fe<sub>2</sub>O<sub>3</sub> in the blast-furnace charge. Howland was motivated to show why a furnace could operate on low coke consumption in violation of "Gruner's ideal working," which was and still is accepted as the most efficient blast-furnace reduction.

I believe the real issue in Mr. Martin's paper is raised by his use of the words "solution loss," which is immediately considered as the solution of carbon in the furnace shaft according to the reaction:



In Howland's paper it was indicated that the carbon gasified at the tuyeres varies in all 26 furnaces, but that the difference between the carbon gasified at the tuyeres and the total to the gas is nearly a constant, indicating that in American blast-furnace practice there is a definite amount of carbon burned *above* the tuyeres in some or other form of chemical reaction.

We should not confuse furnace efficiency with coke consumption. Our only argument is borne out in actual practice, that coke consumption in Lake ore practice may be lower than any theoretical figure possible through the use of Gruner's "ideal working." The over-all efficiency may not be as great, for as long as blast heat is generated from carbon monoxide gas in stoves running at less than 100 per cent efficiency it can hardly be said that such loss in efficiency could be overlooked in comparison with 100 per cent efficiency of carbon monoxide used in the shaft of the furnace.

Such low coke consumption would probably not be possible were it not for the availability of low-ash, low-sulphur, high-volatile Kentucky coals, used in modern by-product ovens. Such coals produce a strong, porous, free-burning coke, which is burned in a minimum of time, thus giving greater concentration of heat in a given

\* Blast Furnace Superintendent, Wisconsin Steel Works.

<sup>15</sup> W. E. Brewster: Carbon in Pig Iron. *Trans. A.I.M.E.* (1936) **120**, 134.

volume than heretofore has been possible. Easily reducible Lake ores, together with lower blast volumes, have utilized this inherent feature of such coke to the end of lower coke consumption.

Most of the discussions of this problem have been concerned with thermochemistry balances. Few have worked out carbon balances. To those who have derived the latter, it is apparent that other refuge than Gruner's theorem becomes necessary. (See furnaces 9-13-15, p. 143 of ref. 15.)

It is true that top gases in all furnaces still show excess reducing power. With CO-CO<sub>2</sub> equilibrium in top gases, the reduction of Fe<sub>2</sub>O<sub>3</sub> by CO becomes reversible, and the predominance of CO becomes necessary to prevent it.

Mr. Martin's conclusions might be summarized as follows:

1. Lower coke consumption than possible under Gruner's "ideal working," may be obtained in the blast furnace.

2. Thermal deficiency, within certain limits, caused by solid carbon reduction of Fe<sub>2</sub>O<sub>3</sub> may be compensated with hot blast.

Probably the most interesting in Mr. Martin's findings are the blast temperatures necessary for varying percentages of direct reduction. These are interesting to the blast-furnace operator in determining whether or not he is justified in providing more or less stove capacity. With a given coke and an ordinary Lake ore burden, the blast-furnace operator can do little to change his blast-furnace reactions. If direct reduction takes place to a great extent, he must either provide sufficient blast heat or be content to cut his ore-coke ratio to the point where hearth temperatures can be maintained. Roughly, any straight ore burden, without scrap, that makes for coke consumption of 1700 lb. or under (coke of 90 to 91 per cent fixed carbon) must, from practical observation, require blast heat to compensate for thermal deficiency due to the endothermic nature of the direct reduction process. On the other hand, how many operators have wondered why additional blast temperature failed to reduce coke consumption below 2000 lb. if practice was generally high, and no other contributing factors apparent.

From our observation, furnaces running on low coke consumption and a correspondingly high percentage of direct reduction are harder to operate on an even keel, of uniform analysis, etc., for once the smooth operating tempo is upset, conditions promoting direct reduction do not exist, and it becomes necessary to decrease the ore-coke burden ratio before such favorable conditions are restored, if sufficient blast temperature cannot be secured or used to restore an upset thermal equilibrium.

Under present operating conditions in modern furnaces, it is not possible to obtain a decreased coke consumption through a nearer approach to Gruner's "Ideal Working." We have shown furnaces under actual operating conditions that had insufficient carbon available to make the "ideal working" possible. We believe Mr. Martin has added some valuable data showing why such "phenomena" are possible and he has given us something tangible in the form of charts 2, 3 and 4, showing a relationship between blast temperature, carbon required for indirect and direct reduction in varying percentages sufficient to satisfy the thermal requirement of the blast furnace.

P. R. NICHOLS,\* South Chicago, Ill.—The work involved in correlating the data presented indicate complete understanding of the various problems of metallurgical calculations as related to the iron blast furnace. In Table 4 the author demonstrates that any practice utilizing direct reduction in excess of 2.3 per cent encounters a deficiency of heat as supplied by the fuel carbon. In so far as this deficiency can be met by the hot blast, it would seem that direct reduction is desirable.

At the Wisconsin Steel Works, we have been convinced for a number of years that the reduction of iron oxides by carbon direct was necessary in order to explain low coke

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\* Assistant Superintendent, Blast Furnace Dept., Wisconsin Steel Works.

practice. As early as 1916, H. P. Howland proved (ref. 12) that a certain amount of direct reduction was essential. Subsequent calculations on our own practice have substantiated the truth of his contentions.

We have all seen furnaces working on very low coke rates as a result of a high percentage of direct reduction. Quite suddenly this practice may take a turn for the worse out of all proportion to any slight increase in burden ratio. Usually a sharp increase in blast temperature will act to restore more direct reduction and the furnace will straighten out as equilibrium is again restored.

We believe that each furnace will strike a balance within itself as to the proportion of direct reduction it can maintain, established by several factors, such as:

1. Quality of coke, primarily as related to the rate of combustion. Coke produced from certain grades of coal lends itself more readily than other cokes to direct action on the oxides of iron.

2. Maintaining a more uniform flow of material into the bosh. Continuous application of the blast without the usual slackening of the wind when stopping the tapping hole after the cast contributes to the amount of direct reduction the furnace can maintain. Brewster (ref. 15) presented data establishing the fact that higher temperatures were obtained as well as more direct reduction in furnaces that were equipped for stopping the iron notch without disturbing the uniform descent of the material into the bosh.

3. Peripheral distribution of the gas stream has been shown by H. W. Johnson<sup>16</sup> to be of equally great significance.

In comparing the various methods of the reduction process on a thermal basis, Mr. Martin evidently has based his calculations at a common temperature level. Inasmuch as these results are used for comparison between the various reduction processes, no criticism can be made concerning the varying thermal requirements of the equilibrium conditions at actual furnace temperatures.

J. S. FULTON, \* Pittsburgh, Pa.—The writer has recently completed a study of the gas production reported on various blast furnaces and has been able to develop curves of gas production and blast requirements that are consistent between 1400 and 6000 lb. of carbon per long ton. These curves are straight lines advancing in some proportion of the carbon rate and are similar to the conventional Brassert curves. No attempt was made to study the metallurgical or thermal reasons why certain weights of C in CO and C in CO<sub>2</sub> in the top gas were found. The curves are a graphical statement of the average production of top gas including CO and CO<sub>2</sub> and the average demand of standard air for the blast. It was found that the CO:CO<sub>2</sub> ratio  $\left( \frac{\text{C in CO}}{\text{C in CO}_2} \right)$  and the amount of direct carbon reduction was a function of the carbon rate.

For any particular furnace operation, the analysis of the top gas will show the final combination of the carbon and the oxygen. From a study of published gas analyses the writer has found that the carbon calcined from the limestone very nearly equals the carbon required in the pig iron and in the flue dust, so the general statement can be made that the weight of carbon charged per ton will appear in the top gas.

The oxygen in the top gas will come from: (1) the ore, usually Fe<sub>2</sub>O<sub>3</sub>; (2) the blast; (3) the oxygen calcined from the limestone; (4) the water vapor disassociated, no matter in what form this water enters the furnace.

The oxygen in 1, 3 and 4 will be grouped under the heading of oxygen in "reducible solids." It is then possible to set up an equation for the chemical balance between the carbon and oxygen in the top gas, as follows:

$$\begin{aligned} \text{O}_2 \text{ in CO} + \text{O}_2 \text{ in CO}_2 - \text{O}_2 \text{ in "solids"} &= \text{O}_2 \text{ in blast} \\ \text{Wt. C in CO} \times \frac{1}{12} + \text{Wt. C in CO}_2 \times \frac{3}{12} - \text{O}_2 \text{ in solids} &= \text{O}_2 \text{ in blast} \end{aligned}$$

<sup>16</sup> Meeting of Amer. Iron and Steel Institute, May 26, 1938.

\* Special Representative, Ingersoll Rand Co.



If the conventional Brassert curves are replotted against pounds of carbon per long ton of iron, the different values of the top gas and blast are shown for rates between 1400 and 2800 lb. of carbon per long ton.

The following values are found at 32°F. and 14.7 lb. abs. for an 1800-lb. carbon rate.

Cubic feet of top gas per long ton.....	136,500
Cubic feet CO, $0.265 \times 136,500$ .....	36,100
Cubic feet CO <sub>2</sub> , $0.128 \times 136,500$ .....	17,500
Cubic feet H <sub>2</sub> , $0.0355 \times 136,500$ .....	4,850
Cubic feet O <sub>2</sub> from H <sub>2</sub> O.....	
Cubic feet blast.....	98,000
Cubic feet O <sub>2</sub> , $98,000 \times 0.21$ .....	20,600

Since 1 lb. of carbon makes 29.63 cu. ft. of either CO or CO<sub>2</sub>, there are

$$\begin{aligned}
 \text{Pounds C in CO} &= \frac{36,100}{29.63} = 1210 \\
 \text{Pounds O}_2 \text{ in CO} &= 1210 \times \frac{16}{12} = 1613 \\
 \text{Pounds C in CO}_2 &= \frac{17,500}{29.63} = 590 \\
 \text{Pounds O}_2 \text{ in CO}_2 &= 590 \times \frac{32}{12} = 1573 \\
 \text{Pounds H}_2 &= 4850 \times 0.0056 = 27.2 \\
 \text{Pounds O}_2 \text{ from H}_2\text{O, H}_2 \times \frac{16}{2} &= 197.6 \\
 \text{Pounds O}_2 \text{ from blast (20,600} \times 0.0892) &= 1840 \\
 \text{Pounds O}_2 \text{ in ore Fe}_2\text{O}_3 \frac{2240 \times 48}{112} &= 960
 \end{aligned}$$

Substituting these values in the equation on p. 62,

$$\begin{aligned}
 1613 \text{ lb. O}_2 + 1573 \text{ lb. O}_2 - (960 - 198 - \text{"stone"})\text{O}_2 &= 1840 \\
 \text{"stone"} &= 188
 \end{aligned}$$

The blast delivers 1840 lb of O<sub>2</sub> per long ton to be combined with the carbon at the tuyeres, where it burns to CO<sub>2</sub> and immediately reverts to CO. Since there is only 1840 lb. O<sub>2</sub> in the blast, only  $1840 \times \frac{12}{16} = 1380$  lb. C can combine with it to make CO.

This CO, passing upward through the furnace, is diminished by the CO that combines with the O<sub>2</sub> from the "solids" to make the CO<sub>2</sub> generated. As shown in the top gas, it is immaterial how many times  $\text{CO} \rightleftharpoons \text{CO}_2$  has altered, from the tuyeres upward, as only the final combination appears in the top gas. In this case the final average analysis shows

$$\frac{1210 \text{ lb. C in CO}}{590 \text{ lb. C in CO}_2} = \text{CO:CO}_2 \text{ ratio} = 2.05$$

The hydrogen disassociated by the carbon from the blast at the tuyeres (only about  $\frac{1}{3}$  the amount shown above) is a very active reducing agent and so can pick up O<sub>2</sub> from the "solids." The very fact that hydrogen appears in the top gas removes it from any consideration as a reducing agent.

There is not enough CO produced at the tuyeres to furnish the minimum commercial metallurgical requirements for the reduction of the ore throughout the furnace, so the remainder of the reduction must be "direct" by carbon. Since there is only 1380 lb. of C in CO at the tuyeres,  $1800 - 1380 = 420$  lb. C must provide "direct" reduction somewhere in the furnace.

At this 1800-lb. carbon rate, the CO:CO<sub>2</sub> ratio in the top gas is 2.05, which is considerably in excess of Gruner's ideal rate of 1, but probably more economical, as



Mr. Martin points out. The Brassert curves at two other points show that the CO:CO<sub>2</sub> ratio at a 1400-lb. carbon rate is

$$\frac{870\text{C in CO}}{530\text{C in CO}_2} = \text{CO:CO}_2 \text{ ratio} = 1.64$$

and at a 2800-lb. carbon rate the ratio is

$$\frac{2270}{530} = \text{CO:CO}_2 \text{ ratio} = 4.28$$

While these figures show that the average furnace advances its CO:CO<sub>2</sub> ratio with an increased carbon rate, it must be noted that the C in CO<sub>2</sub> is 530 lb. at both 1400 and 2800 lb. rate and 580 lb. at an 1800-lb. carbon rate. If these weights of C in CO<sub>2</sub> are correct, then at some much higher rate the C in CO<sub>2</sub> would be zero if the trend of these three rates were followed. The published results contradict this, so undoubtedly there is some error in the trend of the Brassert CO and CO<sub>2</sub> curves.

The Brassert curves show a straight-line increase in volume of top gas and blast and the difference in volume between top gas and blast must be made up by CO + CO<sub>2</sub>, also a straight-line function. The nitrogen in the top gas is furnished by the blast and so need not be considered. While there is 3.55 per cent H<sub>2</sub> by volume, it amounts to only about 0.25 per cent by weight and need not be considered.

The percentage relation between two straight-line relations must be a curve. When the original Brassert paper is studied, it is found that the percentage volume of CO could also be plotted as a curve, flattening out above a 2000-lb. carbon rate and dropping below this rate, but agreeing with the value at 1400-lb. rate. The CO<sub>2</sub> curve is opposite in trend.

Replotting the CO and CO<sub>2</sub> percentages gives the following comparison.

	1400°		1800°		2800°	
	F	B	F	B	F	B
Pounds C in CO <sub>2</sub> .....	530	530	552	590	607	530
Pounds C in CO.....	870	870	1,248	1,210	2,193	2,270
CO:CO <sub>2</sub> ratio.....	1.64	1.64	2.27	2.05	3.60	4.28
Pounds C reduction.....	343	343	400	420	540	660
Percentage C reduction.....	24.6	24.6	22.2	23.3	19.3	23.6

It must be recognized that curves like the Brassert are plotted from the average of many results, so that for any carbon rate the exact weight of C in CO or CO<sub>2</sub>, the weight of O<sub>2</sub> from the "solids" and the weight of O<sub>2</sub> from the blast will vary, and so change both the CO:CO<sub>2</sub> ratio and amount of direct reduction just shown.

Probably a particular furnace operation at an 1800-lb. carbon rate will show exact values different from those shown on pages 33 and 50, but these departures do not destroy the logic of this method of analysis of CO:CO<sub>2</sub> ratio and direct carbon reduction.

In general both the CO:CO<sub>2</sub> ratio and weight of C in "direct" reduction will increase with the increase in carbon rate and in some proportion to it.

The writer congratulates Mr. Martin on his paper, and particularly on defining what CO:CO<sub>2</sub> ratio he uses (i.e.,  $\frac{\text{C in CO}}{\text{C in CO}_2}$ ) for this term is too often used without definition.

## Effect of the Volume and Properties of Bosh and Hearth Slag on Quality of Iron

By G. E. STEUDEL\*

(Cleveland Meeting, April 1939)

THE study of the possibility of effecting a lower cost in the manufacture of pig iron reveals the importance of the ever present question of slag chemistry and volume.

Factors that determine slag chemistry and volume are the impurities in the ore available, the ash-sulphur content of the coke, and a flux material necessary to promote removal of sulphur. Of these, the ores present by far the major source of impurities and what may prove to be the lowest practical slag volume with desired chemistry in one locality may be considered low or high in some other center of iron manufacture. The Chicago district is not only blessed with ores of high quality, but with excellent coke and flux materials as well. It is the intent of this paper to discuss slag problems at the South Works only, where burdens consist of Mesabi ores, Michigan stone, and coke ranging from 7 to 9 per cent ash and containing an average of 0.57 per cent sulphur.

Early in the development of modern blast-furnace practice, the consideration of slags was secondary to the many adjustments of mechanical difficulties, such as furnace lines, stock distribution, stove design for obtaining higher blast temperatures, improved chemical segregation and size of raw materials. Furnace operators, after making these improvements, turned their attention to the study of other refinements in practice, of which slag chemistry appeared to be the most important.

It is only within the last two decades that operators have become familiar with the various aspects of slag compositions. The industry, while rather slow in its recognition, is indebted to such investigators as Rankin,<sup>1</sup> Wright,<sup>1</sup> Feild,<sup>2</sup> Royster,<sup>2</sup> McCaffery,<sup>3</sup> Kinney,<sup>4</sup> Holbrook,<sup>5</sup> and Joseph,<sup>5</sup> whose researches concerning the elimination of sulphur within the blast furnace and the effect of slag composition upon melting point, viscosity, and desulphurizing power have established criteria for the selection of slags of the requisite quality.

Large slag volumes result in higher coke consumption and cost of disposal. Any attempt to lower slag quantity must be accomplished

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Manuscript received at the office of the Institute May 2, 1939. Issued as T.P. 1108 in METALS TECHNOLOGY, September 1939.

\* South Works, Carnegie-Illinois Steel Corporation, Chicago, Ill. Became a member of the A.I.M.E. in July 1939.

<sup>1</sup> References are at the end of the paper.

by a careful adjustment of slag quality in order to produce iron within specifications.

To determine the proper slag quality it is necessary to keep in mind that all blast furnaces in the process of making iron produce two distinct types of slag within the furnace—that which is made above the tuyeres, and that which is formed after fusing with the coke ash below the tuyeres. The slag above the tuyeres contains, naturally, a higher proportion of bases, and should possess a low viscosity and melting point to ensure regular furnace movement and low fuel consumption. The more acid slag below the tuyeres should possess enough calcium oxide at temperatures to warrant sufficient superheat, and a viscosity of ample consistency to ensure a desired desulphurization. From this it can be seen that the optimum slag for the zone above the tuyeres may not prove desirable for the removal of sulphur below the tuyeres and, as a consequence, a compromise in slag composition must be effected. In cases of extreme variation between optimum compositions for the two functions, it has proved advantageous to produce a slag of minimum melting point and viscosity with no regard to the sulphur content of the iron, which is desulphurized by subsequent treatment. The pursuance of this practice at the Corby plant, in England, has resulted in an improved furnace operation and economies that considerably exceed the cost of external desulphurization.

At South Works a balanced slag condition is possible, which permits smooth operation and satisfactory desulphurization within the furnace. Whether or not we are pursuing the most economical method only actual trial will prove.

Table 1 shows average slag analyses and volumes carried in the production of Bessemer and basic grades of iron during the last six months of 1937. These slags will hereafter be referred to as "normal slags." In the plotting of these normal slags on the temperature and viscosity diagrams of the system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  the actual average analyses of the oxides were proportioned to total 100 per cent. Compensation was made for lime equivalent to calcium sulphide by assuming that all the manganese existed as manganese sulphide and the remaining sulphur as calcium sulphide. The results of these adjusted slag compositions are plotted on Fig. 1, the temperature diagram, and Figs. 2 and 3, the viscosity diagrams, at points *A* and *B*, designating the Bessemer and basic hearth slags, respectively. These points reveal that major changes in melting point, viscosity and mineralogical composition are readily effected by slight changes in the chemistry of the burden. Variations of only 2 per cent in lime or silica result in a difference of approximately 200° F. in the melting points of these normal slags. Both points are also near phase-boundary lines, causing continuous mineral changes between calcium orthosilicate, tricalcium disilicate and Gehlenite. The

TABLE 1.—*Average Normal Practice*  
LAST SIX MONTHS OF 1937

Analyses	No. 6 Furnace, Bessemer Iron, Per Cent	No. 8 Furnace, Standard Basic Iron, Per Cent
Actual slag analysis:		
SiO <sub>2</sub> .....	38.5	35.8
Al <sub>2</sub> O <sub>3</sub> .....	10.8	13.7
CaO.....	47.6	44.6
MgO.....	1.5	3.4
S.....	1.11	1.10
Corrected slag analysis:		
Hearth slag:		
SiO <sub>2</sub> .....	39.6	37.1
Al <sub>2</sub> O <sub>3</sub> .....	11.1	14.1
CaO.....	47.8	45.3
MgO.....	1.5	3.5
Bosh slag:		
SiO <sub>2</sub> .....	37.6	35.0
Al <sub>2</sub> O <sub>3</sub> .....	7.0	11.0
CaO.....	54.2	50.5
MgO.....	1.2	3.5
OTHER DATA		
Slag volume (excluding scrap), lb.....	959	1,053
Sinter in burden, per cent.....	0	12.6
Scrap charged per ton metal produced, lb.	18	62
Coke rate, lb. per ton metal.....	1898	1841
Blast temperature, deg. F.....	1188	1152
Blast pressure, lb. per sq. in.....	18.9	19.9
Bases-silica ratio: (actual slag).....	1.27	1.34
Average iron analysis, per cent:		
Silicon.....	1.47	0.92
Sulphur.....	0.028	0.030
Ratio: $\frac{\text{per cent S in slag}}{\text{per cent S in metal}}$ .....	40	37
Grade of iron made.....	100 per cent Bessemer	100 per cent basic
Production:		
Daily tonnage.....	777	994
Percentage of rated capacity.....	94.2	99.4

variations in viscosity, as noted on Figs. 2 and 3, are of equal magnitude, for in this locality the iso-viscosity lines are extremely close together. A slag, whose properties are so greatly influenced by these slight changes in the chemistry of the burden, may lose its effectiveness in the elimination of sulphur.

The theoretical Bessemer and basic bosh slag compositions, indicated upon Figs. 1, 2 and 3 as *a'* and *b'*, respectively, were calculated by deducting oxides in the consumed coke from the oxides present in the actual slags and balancing to 100 per cent after compensating for a

metal siliconization of 75 per cent of normal. As pointed out by McCaffery,<sup>6</sup> the bosh slags may contain a considerable amount of iron oxides, which probably occur as calcium ferrites and iron silicates. The compositions of the bosh slags, as indicated in our calculations, are not

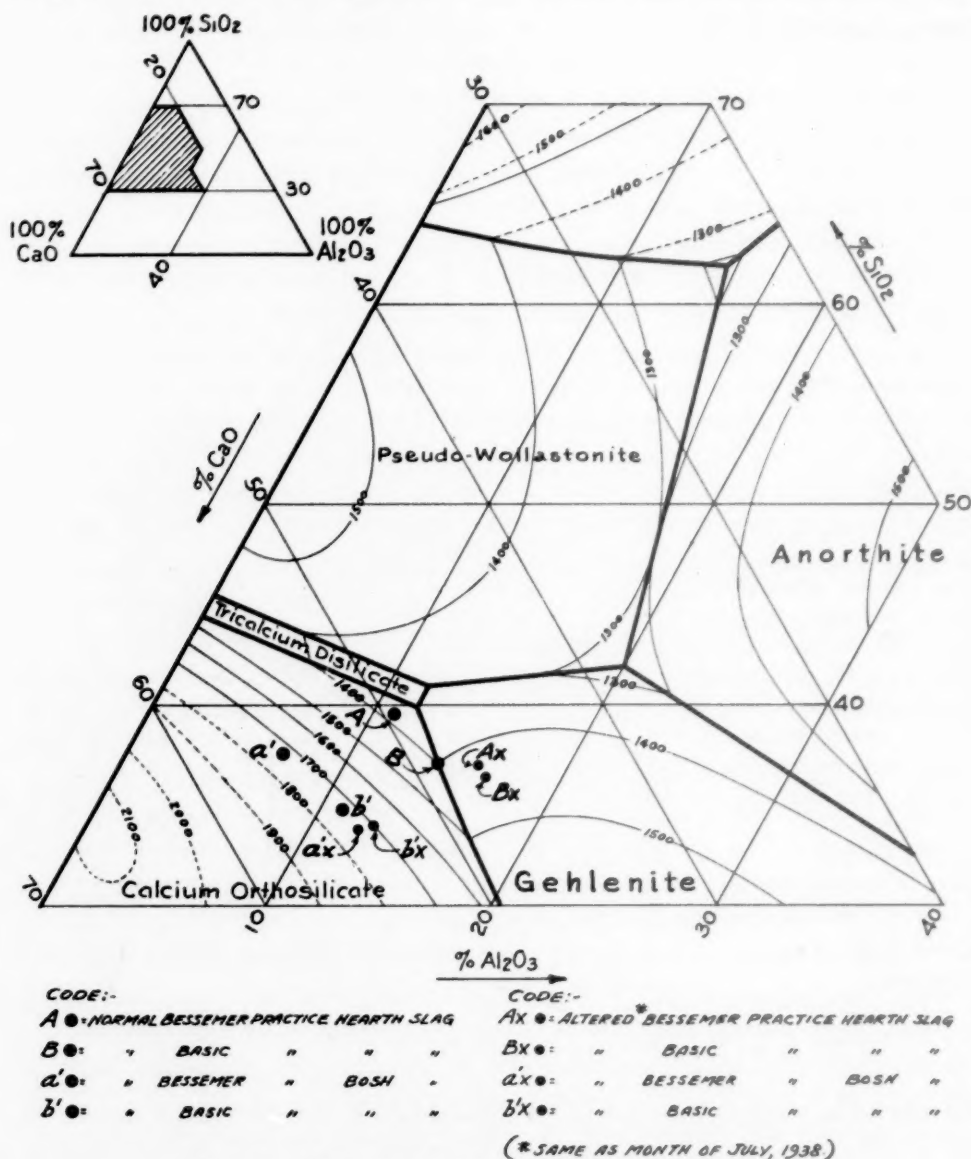


FIG. 1.—LOCI OF NORMAL AND TEST PRACTICE SLAGS.  
Isotherms are in Centigrade units.

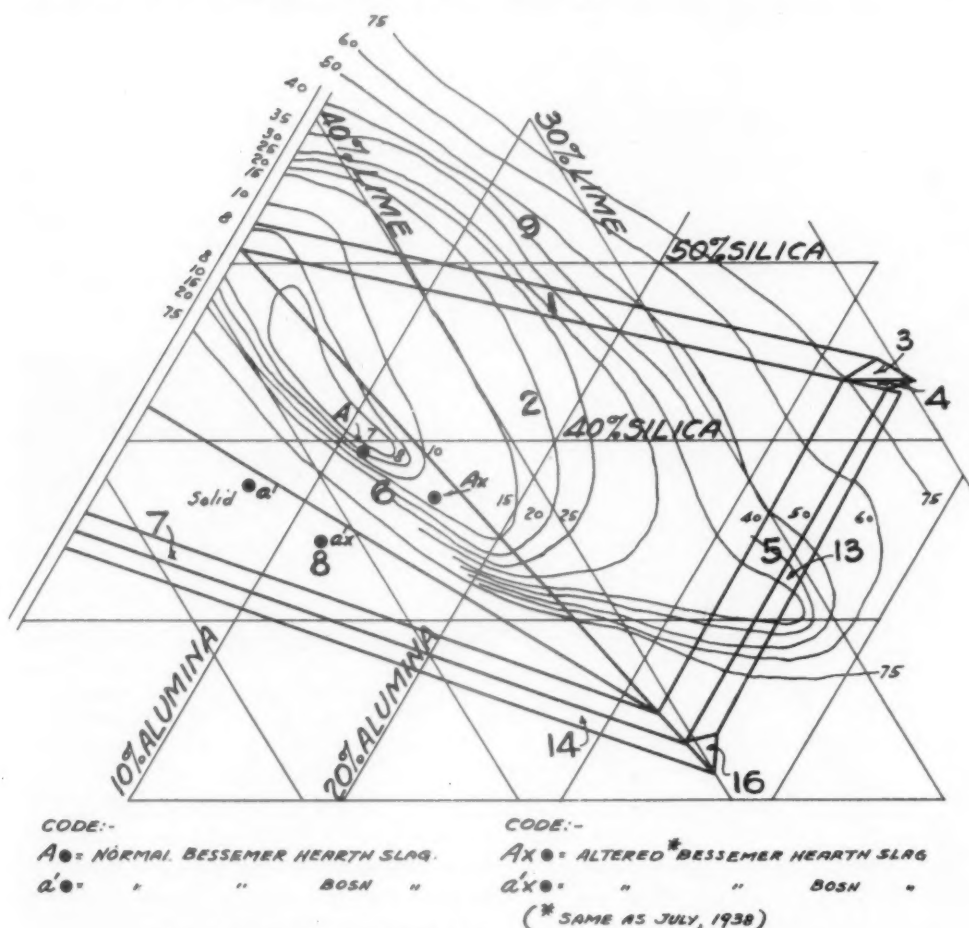
to be construed as those of the actual slags but are merely to be used as guides in estimating the relative thermal and physical characteristics.

An examination of the locations of these slags, which approximate the composition existing above the tuyere zone, indicates that they possess melting points approximately 570° F. higher than the corre-



sponding hearth slags. Viscosities in this region are extremely high (Figs. 2 and 3).

Operating under these slag conditions, small variations in chemistry exert a decided influence upon slag properties and cause wide swings in iron analyses. Such circumstances force the operator to reduce burdens in order to broaden the margin of blast-heat reserve, which leads to lower production and increased coke consumption.



Giving consideration first to the bosh slags for the various stone reductions, we note that  $c'$  lies in a region where melting point and viscosity are much more desirable than those of the normal slag  $b'$ . Fig. 4 indicates that slag  $c'$  has a melting point approximately  $775^{\circ}$  F. lower than slag  $b'$  and Fig. 5 indicates a decided improvement in viscosity. The desirability of a slag of this type over the normal bosh slag has been frequently proved in actual practice by smoother furnace movement and lower coke consumption when operating with lean slags as

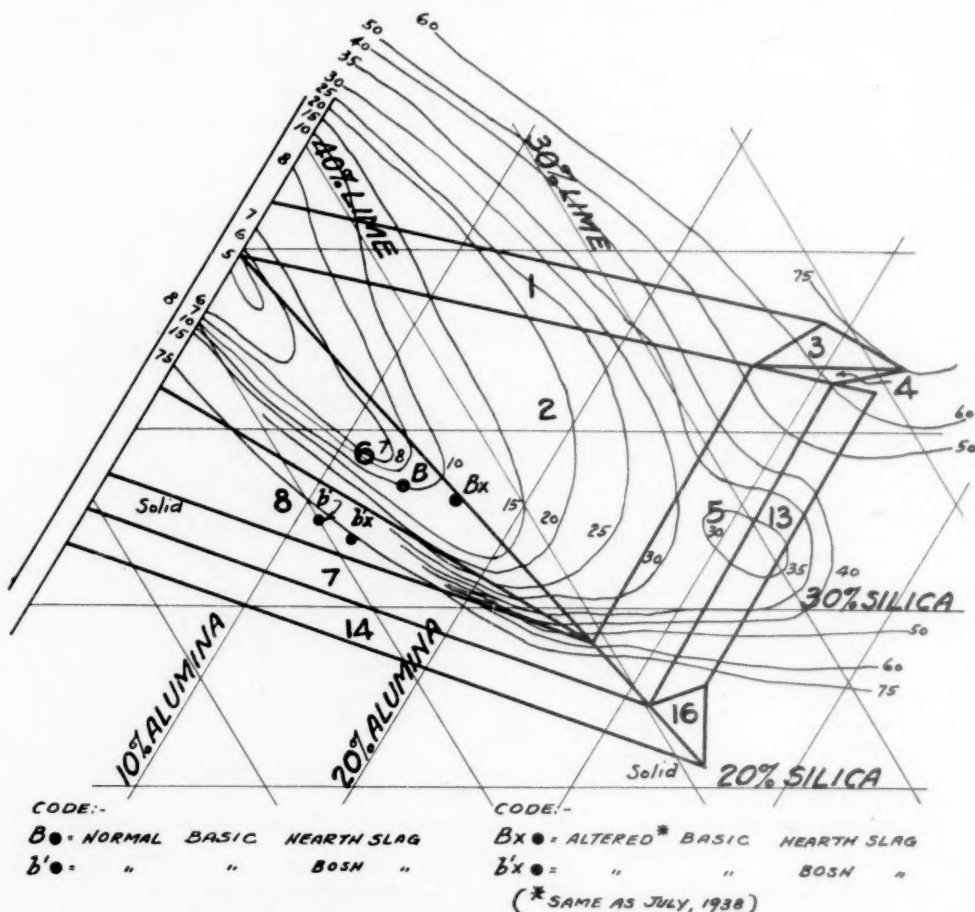


FIG. 3.—VISCOSITIES OF NORMAL AND TEST PRACTICE SLAGS.

compared to the irregular movement and high coke consumption associated with limey slags.

Bosh slags for the higher stone reductions  $d'$  and  $e'$  have melting temperatures comparable to that of  $c'$ . The viscosity of slag  $d'$  is approximately eight poises higher than  $c'$ ; and  $e'$  with the 75 per cent stone reduction is in a very viscous region. Slag  $d'$ , like  $c'$ , shows merit in that it should be a desirable bosh slag. These bosh slags possess superior characteristics over the normal bosh slag and may be expected to produce iron with a favorable reduction in coke consumption. How-

TABLE 2.—Standard Basic Iron

Material	Amount, Lb.	Composition, Per Cent							Slag, Lb.	Stone, Lb.
		Fe	P	Mn	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO		
Gary coke.....	12,000	49	1.08		428	305	50	23	822	1,270
Group 3.....	19,000	9,800	11.20	150.0	966	336	19	19	1,148	2,003
Group 7.....	9,600	4,637	5.38	53.8	1,186	175	11	8	1,302	2,373
Scale.....	500	343	0.09	3.0	8	14	1	1	16	24
Open-hearth slag.....	1,400	315	8.12	82.7	189	35	503	132	870	— 854
Bessemer slag.....	300	59		35.3	169	10	4		185	333
Stone.....	4,750	7	0.24		28	12	2,573	44	2,710	
Total.....	30,800	15,210	26.11	325.8	2,974	887	3,161	227	7,053	5,149

Theoretical stone.....	4,750	Theoretical manganese.....	1.51
Theoretical pig.....	7.02	Fe:C.....	1.27
Theoretical phosphorus.....	0.161	Slag volume.....	1,004

Slag	Con- stituent	Normal Slag Theoretical		25 Per Cent Stone Reduction		50 Per Cent Stone Reduction		74 Per Cent Stone Reduction	
		Oxides, Lb.	Per Cent	Oxides, Lb.	Per Cent	Oxides, Lb.	Per Cent	Oxides, Lb.	Per Cent
Theoretical hearth slag	SiO <sub>2</sub>	2,639	38.1	2,632	42.1	2,625	47.0	2,618	53.2
	Al <sub>2</sub> O <sub>3</sub>	887	12.8	884	14.1	881	15.8	878	17.9
	CaO	3,161	45.8	2,517	40.3	1,874	33.5	1,231	25.0
	MgO	227	3.3	216	3.5	205	3.7	194	3.9
Theoretical bosh slag	SiO <sub>2</sub>	2,295	37.0	2,288	41.4	2,281	46.9	2,274	54.2
	Al <sub>2</sub> O <sub>3</sub>	582	9.4	579	10.5	576	11.9	573	13.6
	CaO	3,111	50.3	2,467	44.6	1,824	37.5	1,181	28.1
	MgO	204	3.3	193	3.5	182	3.7	171	4.1
Slag volume, lb.....		1,004		910		813		715	
Estimated sulphur in metal prod- uct, per cent.....		0.030		0.066		0.144		0.313	

Nomenclature. Loci plotted on Figs. 4 and 5.

Burden	Hearth Slag	Bosh Slag
Normal.....	<i>B</i>	<i>b'</i> *
25 per cent stone reduction.....	<i>C</i>	<i>c'</i>
50 per cent stone reduction.....	<i>D</i>	<i>d'</i>
75 per cent stone reduction.....	<i>E</i>	<i>e'</i>

ever, calculations based on the Holbrook and Joseph diagram of relative desulphurizing power (Fig. 6) indicate that the corresponding hearth slags *C*, *D* and *E* do not possess sufficient desulphurizing power to produce iron within present open-hearth specifications. The estimated sulphur contents of the iron are as follows:

25 per cent stone reduction.....	0.066 per cent sulphur in iron
50 per cent stone reduction.....	0.144 per cent sulphur in iron
75 per cent stone reduction.....	0.313 per cent sulphur in iron

Because of the small amount of research in these particular fields with actual furnace slags, the estimated sulphur contents are to be taken only as an indication of what might be expected.

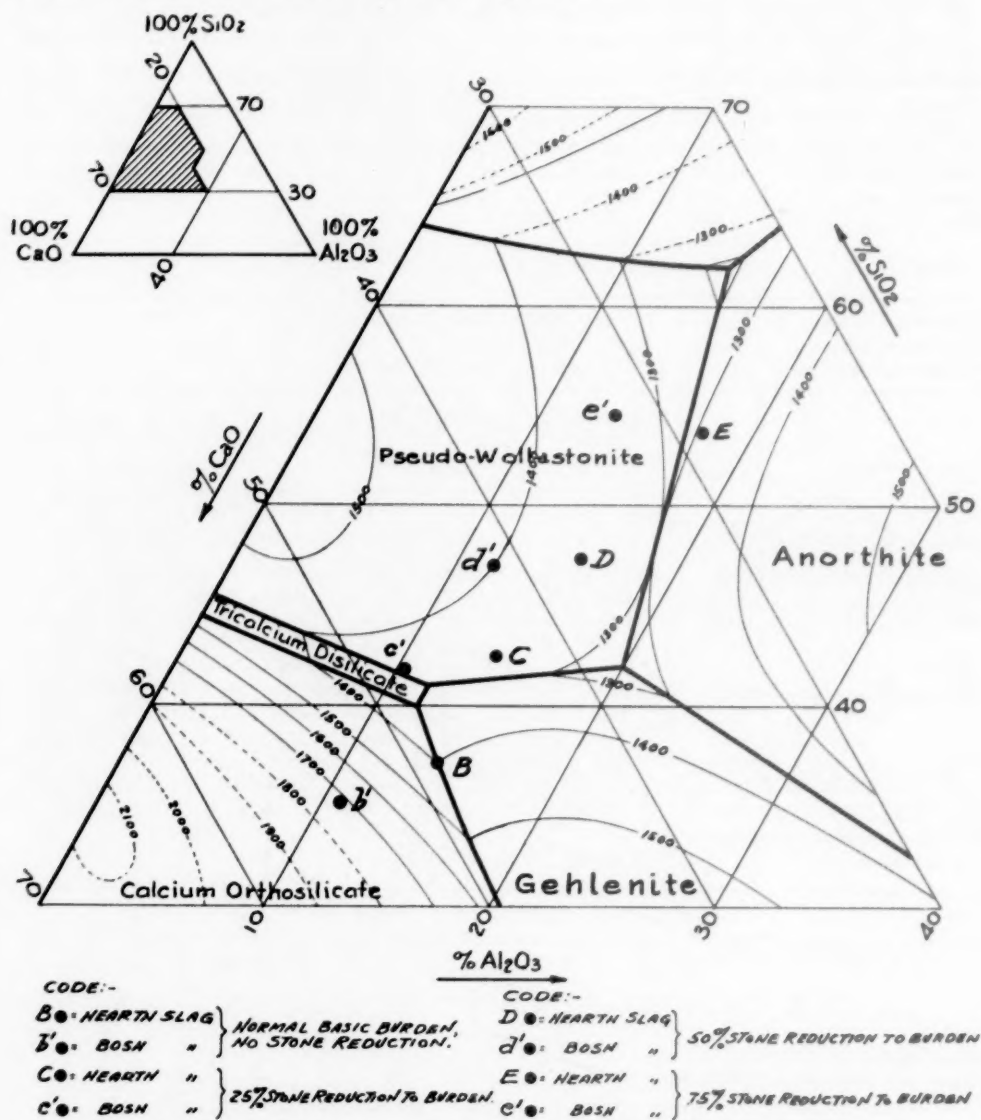
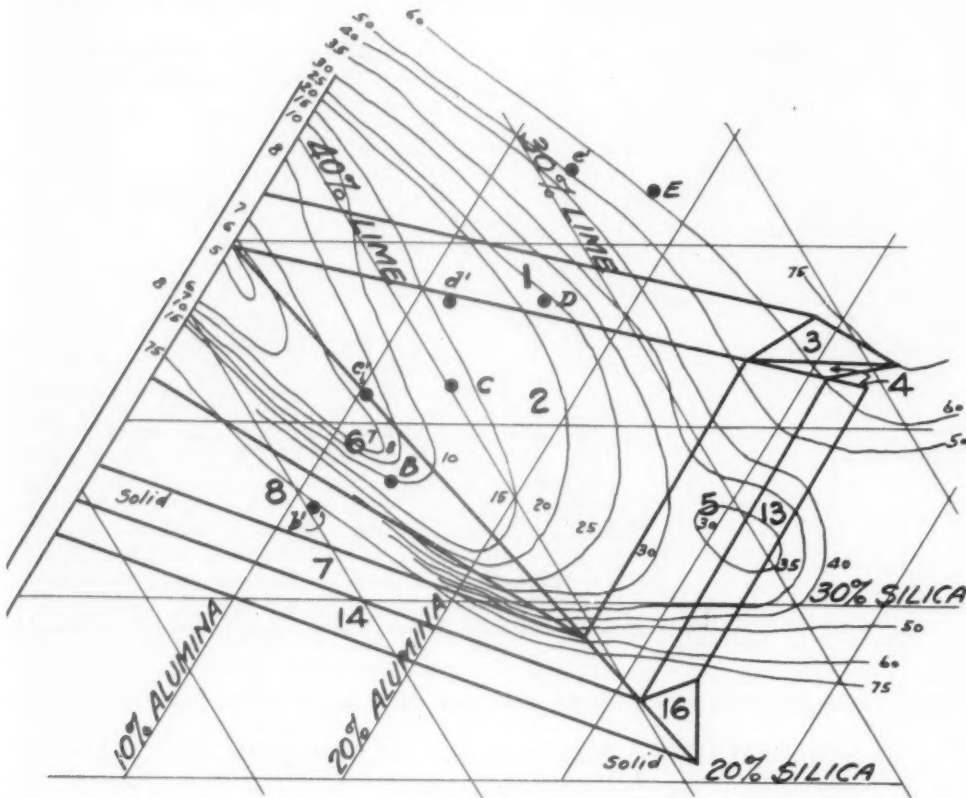


FIG. 4.—SLAGS AT VARIOUS LIMESTONE REDUCTIONS IN A BASIC BURDEN.

Whether or not the savings obtained with the suggested method for improving bosh slags would be enough to justify external desulphurization, we are not in a position to state without further investigation. The study of leaner slags did, however, lead to a proposal that appears to have possibilities. This consists of the injection of preheated calcium oxide into the hearth or lower part of the bosh in a manner similar to the Heskamp flue-dust injection process. A removal of approximately 25 per cent stone from the burden and the compensating addition of an

equivalent amount of calcium oxide to the hearth would retain the advantageous characteristics of the leaner bosh slag and eliminate the necessity for external desulphurization. Calculations indicate that if the calcium oxide were preheated to a temperature of 1700° F. the heat necessary to bring the oxide to that of the normal hearth temperatures would be supplied by an addition of approximately 22° F. blast temperature.



CODE:-

B●: HEARTH SLAG	} NORMAL BASIC BURDEN, NO STONE REDUCTION	D●: HEARTH SLAG	} 50% STONE REDUCTION TO BURDEN.
B'●: BOSCH "		D'●: BOSCH "	
C●: HEARTH "	} 25% STONE REDUCTION TO BURDEN.	E●: HEARTH "	} 75% STONE REDUCTION TO BURDEN.
C'●: BOSCH "		E'●: BOSCH "	

FIG. 5.—VISCOSITIES OF SLAGS AT VARIOUS STONE REDUCTIONS IN BURDEN.

Because mill conditions did not permit any of the drastic changes in practice described above, our attention was diverted to a more conservative experimental plan in which available materials and equipment could be utilized.

Having located the normal Bessemer and basic slags, A and B, upon the diagram (Fig. 1), slag location may be improved by moving to the right, that is, to a position within the upper area of the Gehlenite field.



The attainment of a slag approximating such a position required an increase in the alumina content. To achieve this, we had but one alternative, which, fortunately, served a twofold purpose. Since approximately half the alumina in the burden comes from the coke, it was apparent that if the slag volumes were reduced the alumina would increase. Theoretical slag compositions were calculated for burdens in which the siliceous ores were eliminated. The compositions of such slags approximate those plotted upon Figs. 1, 2 and 3 at points *Ax*, *Bx*, *a'x* and *b'x*.

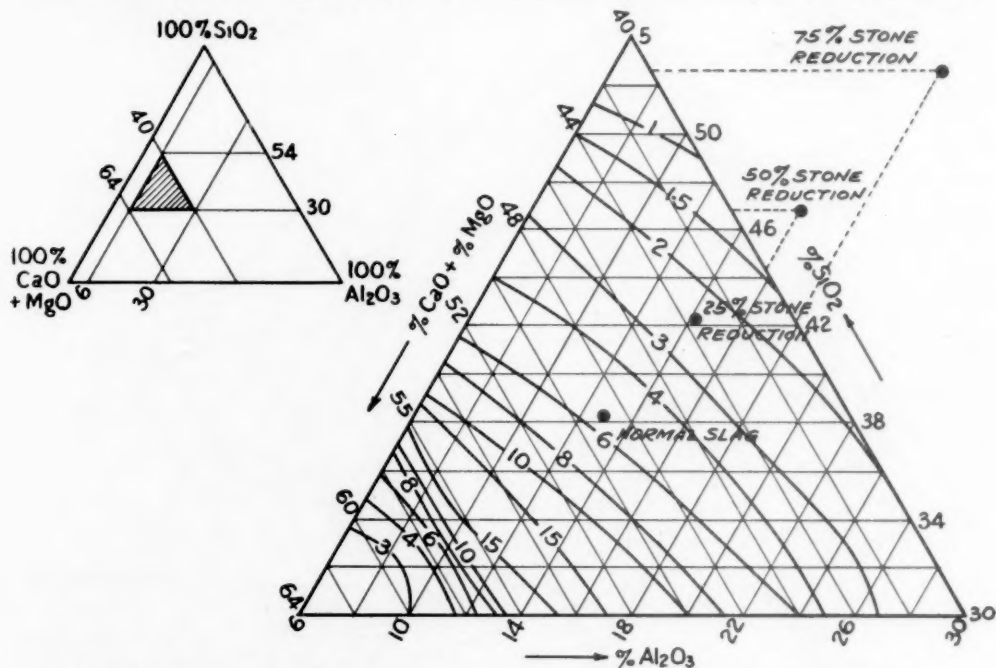


FIG. 6.—DESULPHURIZING POWER OF SLAGS WITH REDUCED STONE IN BURDEN.

The locations of these slags are a decided improvement over those of the normal slags. The melting temperatures and the viscosities of the hearth slags are much less subject to rapid changes due to slight variations in burden chemistry. The isotherms indicate that changes of about 5 per cent in hearth-slag compositions are required to cause a difference in melting temperatures of approximately 200° F., whereas the same temperature difference is effected by a change of but 2 per cent in the normal slag composition. As previously mentioned, the essential difference between the slags is in their alumina content. Slag *Bx* contains approximately 16 per cent alumina, while the normal basic slags contain 14 per cent or less. In the normal Bessemer practice the alumina is rarely above 11 per cent, but with the reduced slag volume and the charging of an additional 200 lb. of producer ash it was possible to obtain slags approximating 16 per cent alumina.

The bosh-slag locations, which approximate those of the altered practice-slag compositions, indicate relatively little improvement in

TABLE 3.—*Test Practice, No. 6 Blast Furnace, Bessemer*

	Feb. 1938	March 1938	April 1938	May 1938	June 1938	July 1938
ACTUAL SLAG ANALYSIS, PER CENT						
SiO <sub>2</sub> .....	37.57	37.93	37.25	36.97	37.30	35.68
Al <sub>2</sub> O <sub>3</sub> .....	13.82	13.78	13.66	15.07	14.26	15.72
CaO.....	44.77	44.62	45.78	44.77	45.16	45.00
MgO.....	2.09	1.93	1.82	1.60	1.74	2.02
S.....	1.14	1.15	1.21	1.27	1.35	1.37
CORRECTED SLAG ANALYSIS, PER CENT						
SiO <sub>2</sub> .....	38.8	39.0	38.4	38.2	38.5	36.9
Al <sub>2</sub> O <sub>3</sub> .....	14.2	14.4	14.1	15.6	14.7	16.2
CaO.....	44.8	44.6	45.7	44.6	45.0	44.8
MgO.....	2.2	2.0	1.9	1.6	1.8	2.1
BOSH SLAG, PER CENT						
SiO <sub>2</sub> .....						33.8
Al <sub>2</sub> O <sub>3</sub> .....						12.2
CaO.....						52.2
MgO.....						2.0
Slag volume (excluding scrap), lb.....	921	881	861	770	738	767
Sinter in burden, per cent.....	10.6	1.8	1.0	0.3	0.0	0.0
Scrap charged, lb. per ton metal produced....	12	9	267	232	12	78
Coke rate, lb. per ton of metal.....	1771	1807	1693	1676	1790	1776
Blast temperature, deg. F.....	1132	1155	1125	1210	1235	1147
Blast pressure at blowing engines, lb. per sq. in.	16.8	16.8	17.8	17.4	15.6	15.5
Ratio: $\frac{\text{per cent S in slag}}{\text{per cent S in metal}}$ .....	48	40	63	51	50	53
Ratio: $\frac{\text{Bases}}{\text{Silica}}$ (actual slag).....	1.25	1.23	1.28	1.25	1.29	1.32
Iron analysis:						
Silicon.....	1.47	1.52	1.46	1.40	1.53	1.38
Sulphur.....	0.024	0.029	0.019	0.025	0.027	0.026
Days on various grades of iron:						
Basic.....	0	0	0	0	0	6
Bessemer.....	12	19	20	29	26	22
Ingot mold.....	16	12	10	0	0	0
Malleable.....	0	0	0	2	4	3
Number of changes in grade of iron produced.	4	5	4	6	6	7
Production:						
Daily tonnage.....	671	690	842	868	732	752
Percentage of rated capacity.....	81.3	83.6	101.9	105.2	88.6	91.1

TABLE 4.—*Test Practice*

	No. 8 Blast Furnace, Basic					
	Feb. 1938	March 1938	April 1938	May 1938	June 1938	July 1938
ACTUAL SLAG ANALYSIS, PER CENT						
SiO <sub>2</sub> .....	35.84	36.58	36.18	35.78	35.80	35.30
Al <sub>2</sub> O <sub>3</sub> .....	14.56	13.91	13.96	14.75	15.57	15.89
CaO.....	43.15	43.35	43.77	44.40	43.20	43.25
MgO.....	4.08	3.94	3.71	2.84	3.08	3.20
S.....	1.14	1.07	1.08	1.12	1.18	1.27
CORRECTED SLAG COMPOSITION, HEARTH SLAG, PER CENT						
SiO <sub>2</sub> .....	37.1	37.7	37.4	36.9	37.1	36.6
Al <sub>2</sub> O <sub>3</sub> .....	15.1	14.4	14.5	15.3	16.1	16.5
CaO.....	43.6	43.8	44.3	44.9	43.6	43.6
MgO.....	4.2	4.1	3.8	2.9	3.2	3.3
CORRECTED SLAG COMPOSITION, BOSH SLAG, PER CENT						
SiO <sub>2</sub> .....						33.9
Al <sub>2</sub> O <sub>3</sub> .....						12.9
CaO.....						49.8
MgO.....						3.4
Slag volume (excluding scrap), lb.....	981	938	915	824	786	778
Sinter in burden, per cent.....	11.9	15.2	3.8	3.7	0.0	0.0
Scrap charged per ton metal produced.....	112	113	80	75	84	117
Coke rate, lb. per ton metal.....	1732	1697	1753	1748	1734	1667
Blast temperature, deg. F.....	1003	1024	1109	1020	1046	1155
Blast pressure at blowing engines, lb. per sq. in.....	17.5	17.9	18.4	17.9	17.0	17.9
Ratio: $\frac{\text{per cent S in slag}}{\text{per cent S in metal}}$ .....	41	40	42	45	47	53
Ratio: $\frac{\text{Bases}}{\text{Silica}}$ (actual slag).....	1.32	1.29	1.28	1.25	1.29	1.32
Iron analysis:						
Silicon.....	0.91	0.90	0.89	0.93	0.91	0.94
Sulphur.....	0.028	0.027	0.026	0.025	0.025	0.024
Days on various grades of iron:						
Basic.....	28	31	30	31	30	31
Bessemer.....	0	0	0	0	0	0
Ingot mold.....	0	0	0	0	0	0
Malleable.....	0	0	0	0	0	0
Number of changes in grades of iron produced	0	0	0	0	0	0
Production:						
Daily tonnage.....	980	1066	1071	1076	1041	1129
Percentage of rated capacity.....	98.0	106.6	107.1	107.6	104.1	112.9

physical or thermal properties over the normal slags. Being aware of the extremely viscous condition of the slags in the bosh zone, we felt assured that a reduced quantity of slag would considerably improve gas penetration and furnace movement.

As a result of the foregoing considerations, it was decided to experiment with slag compositions in progressive steps of reduced slag volume on one Bessemer and one basic furnace. The first steps of the six-month test were taken in the month of February 1938.

The pertinent data for the period of the experiment are shown on Tables 3 and 4. Although practice in No. 6 furnace is referred to as "Bessemer" it made ingot-mold grade iron for a considerable portion of the period, as well as merchant and standard basic over short durations, as indicated in the tables.

TABLE 5.—*Comparison of Slag Volumes and Coke Rates*

Furnace	Normal Practice, Last 6 Months of 1937	Test Practice, Average: June and July 1938	Difference
Bessemer:			
Slag volume.....	959	752	-207
Coke rate.....	1,898	1,783	-115
Pounds scrap charged per ton metal produced.....	18	45	+ 27
Per cent sinter in burden.....	0	0	0
Basic:			
Slag volume.....	1,053	782	-271
Coke rate.....	1,841	1,701	-140
Pounds scrap charged per ton of metal produced.....	62	100	+ 38
Per cent sinter in burden.....	12.6	0	- 12.6

In comparing the normal practice with that of the test period, it will be noted that in the practice on the basic furnace a monthly average slag volume of 778 lb. was attained, which was as low as the materials available would permit. In previous practice slag volumes of less than 1050 lb. had never been regularly used. The average monthly slag volume in the Bessemer practice was reduced to as low as 738 lb., whereas in the normal practice 950 lb. was considered minimum.

The improvement of coke rates in the test period is evident. Table 5 shows a comparison of the average slag volumes and coke rates for average normal practice with those of the average for the last two months of the test period, during which the lowest slag volumes were carried. While lower coke rates were attained during the test period than those of the two months shown here, those low rates were accompanied, as examination of the previously tabulated data reveals, by higher

amounts of scrap and sinter in the burdens. The coke reduced per 100 lb. slag volume for the Bessemer practice was

$$100 \times \frac{115}{207} \text{ which gives } 55.6 \text{ lb. per ton metal (including scrap).}$$

Assuming that 300 lb. of coke is required to melt 2240 lb. of scrap in the blast furnace, the melting of 27 lb. of scrap requires:

$$27 \times \frac{300}{2240} \text{ or } 3.6 \text{ lb. coke.}$$

The coke saving in the Bessemer practice then becomes:

$$\frac{(55.6 - 3.6) 2240}{2240 - 27} \text{ or } 52.7 \text{ lb. coke per ton of metal produced (excluding scrap) for each 100 lb. reduction in slag volume.}$$

The saving effected in the basic practice, calculated in the same manner, is 48.4 lb. of coke per ton of metal produced (excluding scrap) for each 100-lb. reduction in slag volume. It is interesting that a substantial reduction in coke consumption was effected in the basic practice in spite of the 12.6 per cent sinter reduction in the burden.

From these data, it appears that the average saving in coke, after adjustment for scrap, may be said to be approximately 50 lb. per ton of metal for every 100 lb. of slag volume reduced.

Blast pressures during the test period were definitely lower and more uniform. There is little doubt that this was due to the smaller amount of viscous slag in the bosh during the low slag volume practice.

The effect of the altered slag chemistry and the slag volume upon smooth furnace operation was very marked, as shown by Figs. 7 to 10. While the basic practice shows a general improvement in sulphur uniformity in iron to the extent of the lowest slag volumes carried, the Bessemer practice indicates an optimum degree of sulphur uniformity at a slag volume of approximately 820 lb. This, however, should not be considered evidence against the lower slag volumes, as the frequency of burden changes required by variations in specifications of iron to meet mill demands increased over the latter months. Through necessity, the test was run under actual operating conditions and because of the low steel demands during the first half of 1938 the burden on the Bessemer furnace was changed from four to seven times per month, and although the burden on the basic furnace remained the same, the wind was reduced or increased 6000 to 7000 cu. ft. per minute from one week to another.

Uniformity in silicon on both the Bessemer and basic practice likewise shows a gradual improvement. Here again, the curves tend to turn upward at the lower slag volumes, apparently for the same reasons as for the trend in the sulphur uniformity curves.

The most outstanding operating advantage in this practice is the consistently high quality of the metal product, which was common



throughout the range of the slags carried during the six-month period of the experiment. During this period the Bessemer furnaces operated for over three months and the basic furnace for over five months without making a cast containing more than 0.050 per cent sulphur. We attribute this improvement directly to the slowness of furnace "swings" charac-

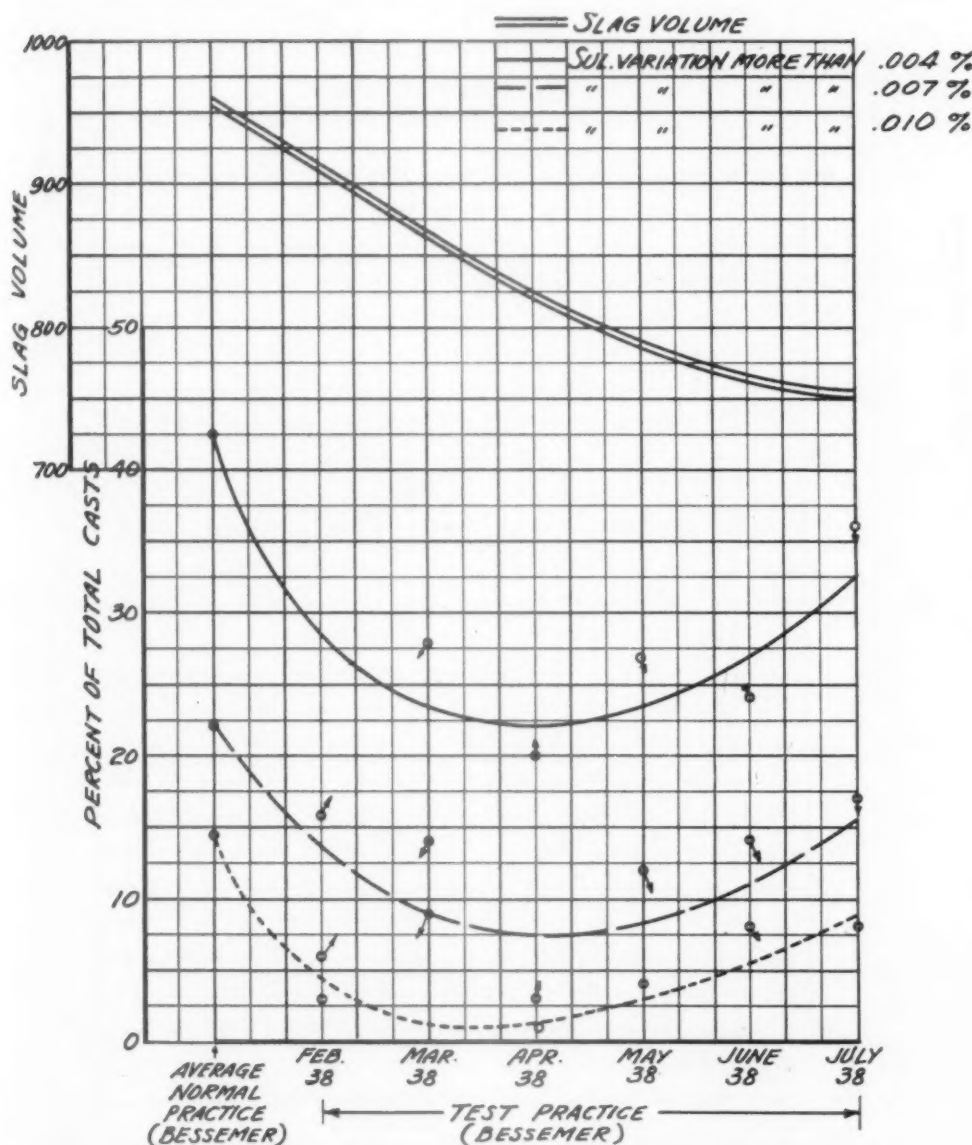


FIG. 7.—CAST-TO-CAST SULPHUR VARIATION IN BESSEMER IRON.

teristic of the test practice, which gave opportunity for the application of a degree of control not heretofore realized. The distribution data on sulphur and silicon analyses are tabulated in Tables 8 and 9. Curves depicting comparisons between the average quality of metal during the normal period and that of the test period are shown on Figs. 11 and 12.

At the beginning of the experiment, there was some doubt as to the practical limit to which slag volumes, even with altered chemistry, could be reduced without detriment to the quality of the iron. The attainment of a uniform, high-quality product was not accomplished without some change in operating practice. To further promote removal of

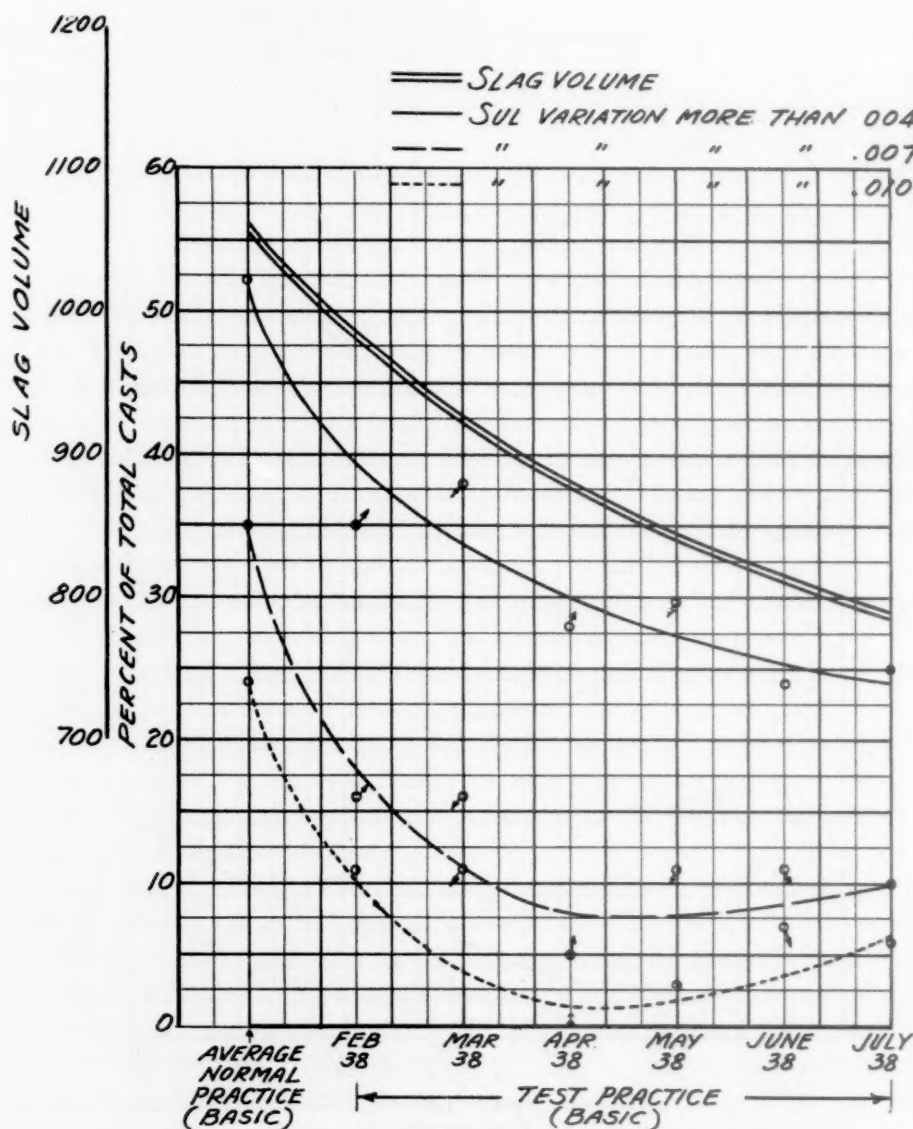


FIG. 8.—CAST-TO-CAST SULPHUR VARIATION IN BASIC IRON.

sulphur from the iron with lower slag volumes, only one flush was made before the cast, and care was taken not to blow the furnace at cast time, but rather to leave as much of the slag in the furnace as practicable. In this way the average time of the slag in the hearth was lengthened, and opportunity for slag-metal contact increased, with the result that the

maximum desulphurizing power of the slag was approached. The marked difference in the sulphur contents of the slags on the Bessemer and basic furnaces might be attributed to the fact that on the Bessemer furnace, which is equipped with a remote-control mud gun, the flow of

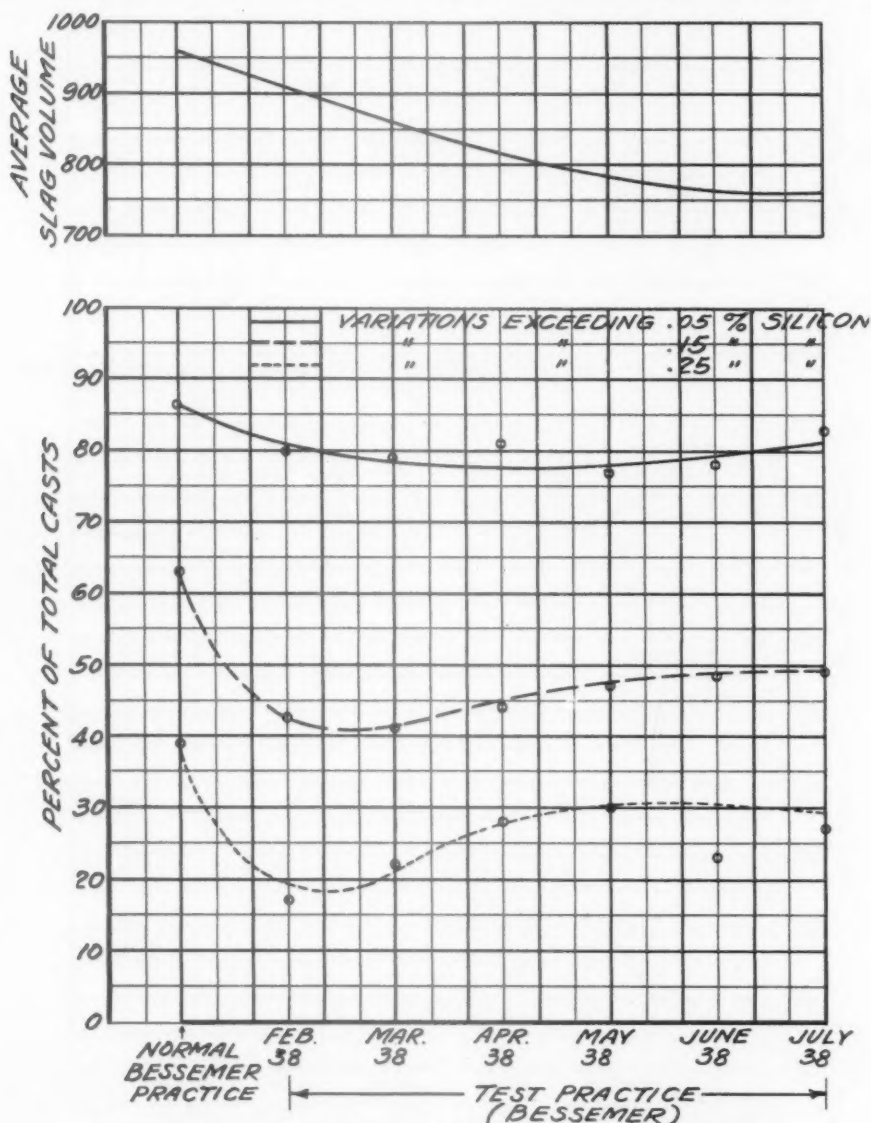


FIG. 9.—CAST-TO-CAST SILICON VARIATION IN BESSEMER IRON.

slag from the tapping hole at cast was more easily regulated, whereas in the basic furnace, which does not have a remote-control gun, as much slag could not safely be retained in the furnace at cast time.

A comparison of the desulphurizing ratio of the slags during the test period with that of the normal period is illustrated in Fig. 13. The results prove conclusively that the limit of sulphur absorption of the slags was not reached.

To continue the practice of low slag volumes necessarily eliminates the use of high-silica ores. What the cost would be to reduce the silica in these ores to permit low slag volumes has not been determined. The

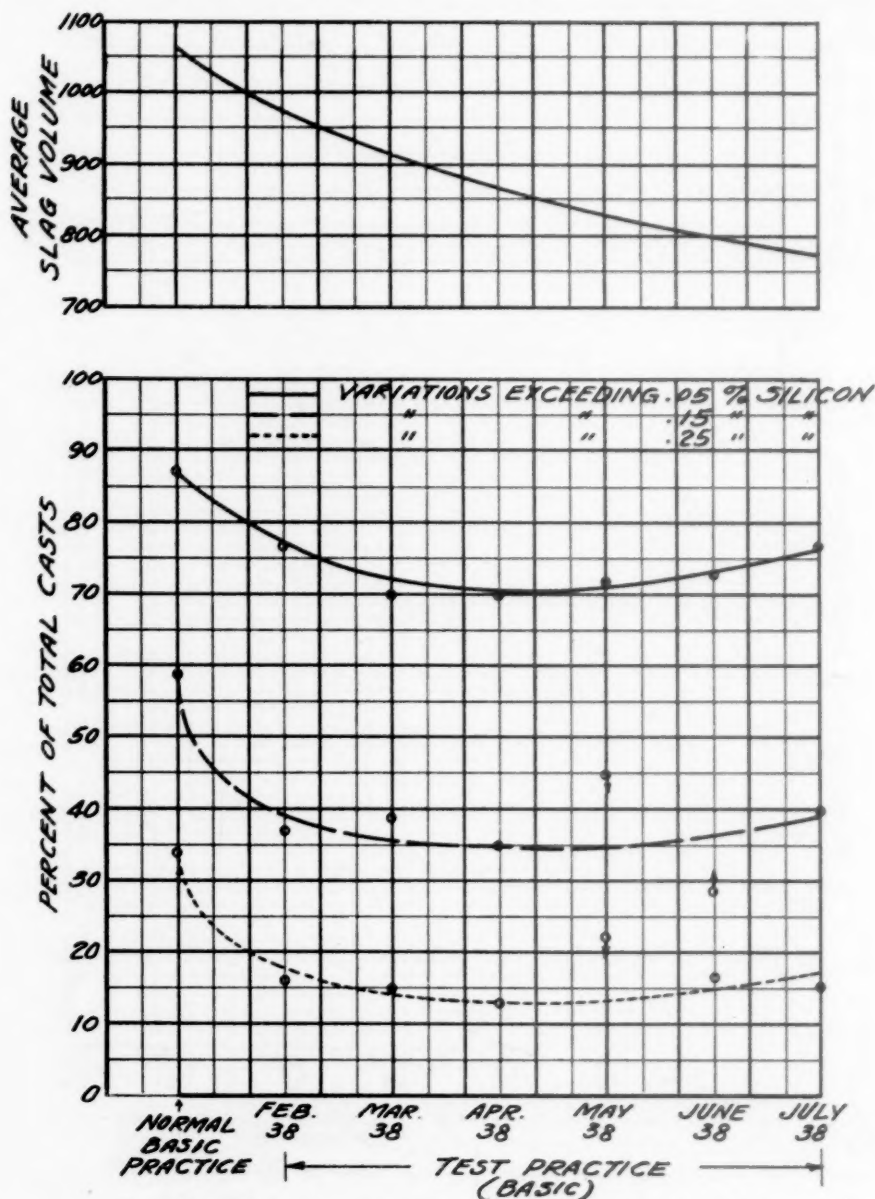


FIG. 10.—CAST-TO-CAST SILICON VARIATION IN BASIC IRON.

removal of the differences in silica and stone between the burdens low and high in slag results in a substantial saving in the freight rates alone.

As the slag volumes are reduced by the elimination of the siliceous ores, the oxides originating from the coke have a measurably increased effect upon the percentage of total oxides in the slag. For this reason,

it is essential that the ash in the coke be kept uniform so that maximum benefits may accrue from the altered slag practice.

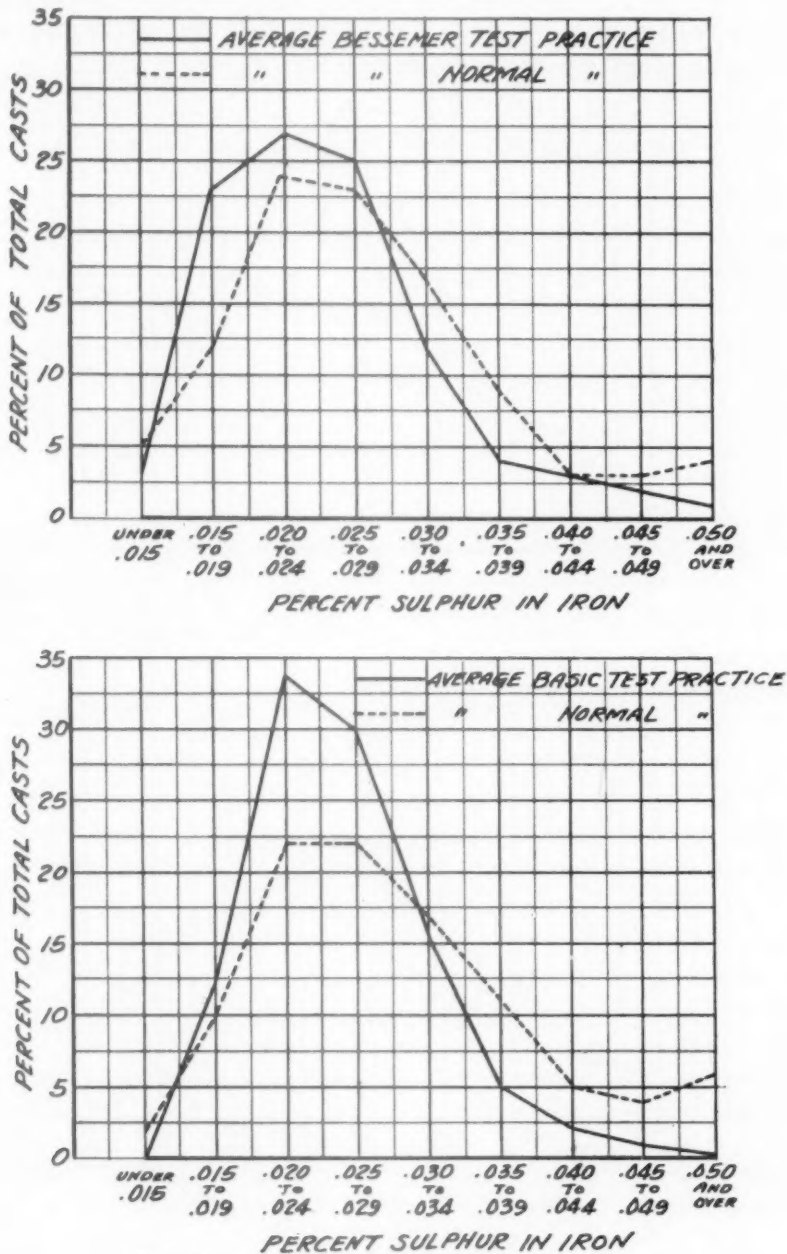


FIG. 11.—DISTRIBUTION OF SULPHUR ANALYSIS.

#### CONCLUSION

The test, while hampered by many changes in burden and wind, was run under regular operating conditions with the furnaces averaging from 92 to 105 per cent of their rated capacity. The changes were not conducive to uniform operation or to low coke practice. This, however, was



partly offset by the more uniform ash content in the coke usually attendant with a low rate of mill operation.

The fact that furnace movement was not at any time disturbed by these many changes is convincing evidence that the lower slag volumes improved the condition of the bosh slag.

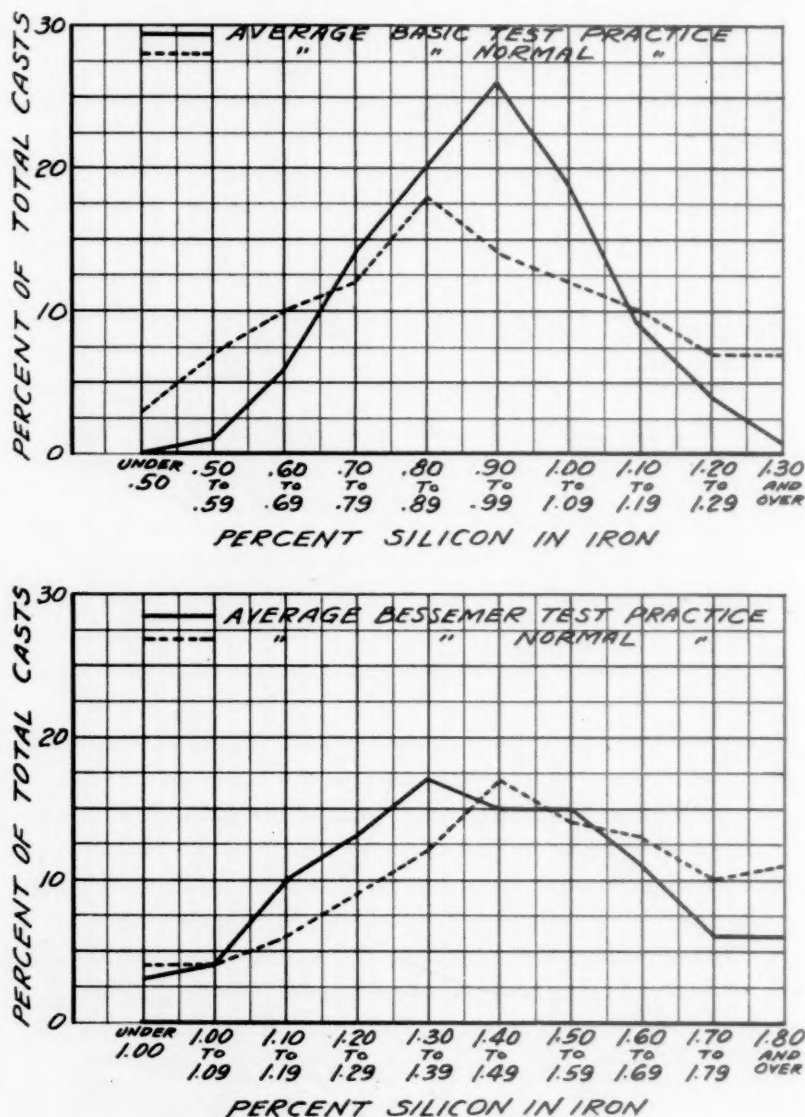


FIG. 12.—DISTRIBUTION OF SILICON ANALYSIS.

Sulphur absorption in the slag was increased approximately 20 per cent by the retention of more slag in the furnace, particularly at cast time, thereby making possible maintenance of a deeper bed and permitting longer contact between iron and slag.

To state any of the cost reductions in dollars and cents would be confusing, as the cost of raw materials varies so widely, owing, primarily,

to shipping rates; practice that would lead to a substantial saving at one plant might be less important at another iron-manufacturing center. The savings that can be directly attributed to the revised practice are itemized as follows: (1) reduced amount of slag for disposal, (2) reduced coke consumption, (3) reduced stone consumption, (4) reduced cost of ore transportation per iron unit effected by elimination of high-silica ore, (5) reduced flue-dust production, (6) lower blowing-engine pressures.

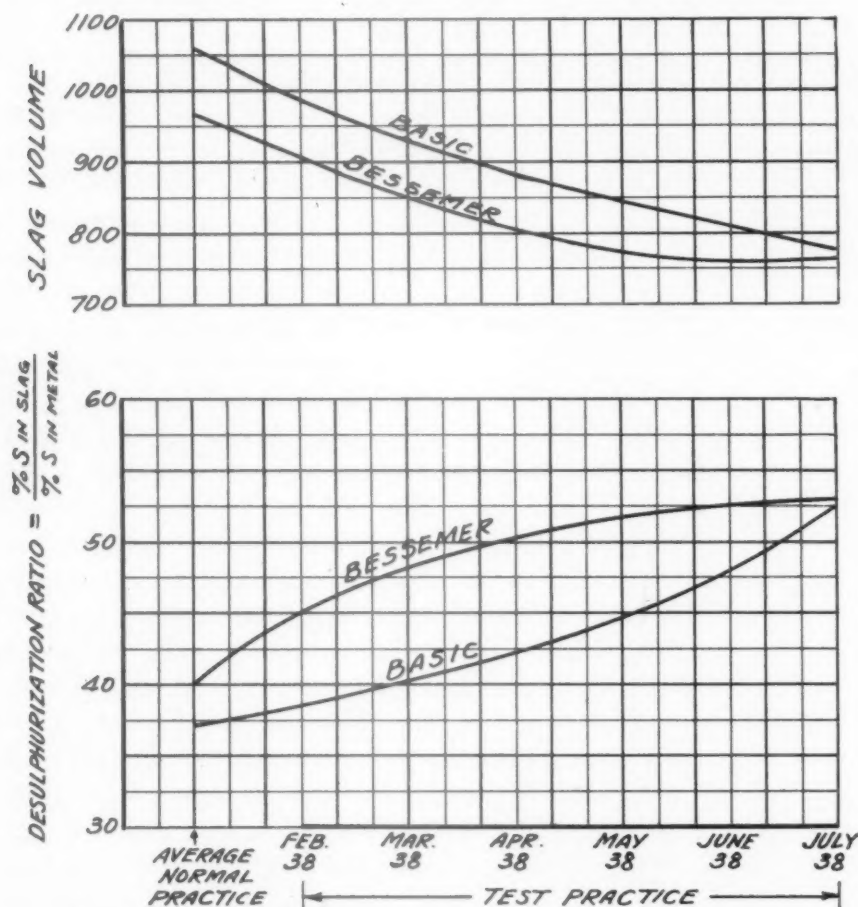


FIG. 13.—DESULPHURIZING RATIOS, NORMAL AND TEST PRACTICE.

To these should be added an indirect saving in a more uniform product for the open hearths, and the ease with which furnace practice can be adjusted to conform with mill production.

#### ACKNOWLEDGMENT

The author wishes to express his appreciation to Messrs. R. D. Beck and C. G. Hogberg, members of the South Works blast-furnace organization, for their generous assistance in the preparation of this paper. He also wishes to thank Mr. H. A. Strain, Assistant General Superintendent,

South Works, and Mr. H. W. Johnson, Superintendent of Blast Furnaces, Inland Steel Co., for their kindly criticism and suggestions.

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## Desulphurization of Pig Iron with Calcium Carbide

BY C. E. WOOD,\* MEMBER A.I.M.E., E. P. BARRETT\* AND W. F. HOLBROOK\*

(Chicago Meeting, October 1939)

THE Blast Furnace Studies Section, Metallurgical Division, Bureau of Mines, has been working for several years on the mechanism of desulphurization of iron and steel by slags. The usual assumption that desulphurization takes place by diffusion of FeS from metal into slag and subsequent reaction of this FeS with CaO to produce CaS has seemed to us inconsistent with a number of experimental results we have obtained. We undertook, for example, to determine the proportion of sulphur in a slag present as FeS. An entirely satisfactory method of doing this has not yet been evolved. The results of extraction with metallic antimony led to an interesting conclusion, however.

FeS is readily soluble in metallic antimony, either physically or by chemical reaction. On the other hand, CaS was found to be insoluble. Hence it would appear that by rapid extraction of the slag with antimony we might expect to determine the distribution of sulphur between iron and calcium. The results showed that much of the sulphur was present as FeS. In some instances the extraction of sulphur as FeS was almost quantitative. For example, in a slag containing 3.8 grams Fe and 3.7 grams S, extraction removed 1.18 grams S and 2.12 grams Fe. If all the iron present in the antimony had been FeS, 1.21 grams S would have been extracted. In another slag with 8.6 grams Fe and 0.06 gram S present, 0.14 gram Fe and 0.08 gram S were extracted. This was obviously extraction of sulphur as FeS within the analytical error and showed that FeS was present either in solution or as a dispersion.

Attempts to determine the solubility of FeS and CaS in slag by quenching and ultramicroscopic investigation have indicated that the solubility of FeS is very low, and that reactions in the slag are probably not to be considered as homogeneous. A more detailed report on these theoretical considerations will be made at a later date.

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Published by permission of the Director, U. S. Bureau of Mines. Manuscript completed June 1939; received at the office of the Institute Aug. 3, 1939. Issued as T.P. 1131 in METALS TECHNOLOGY, December 1939.

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From these preliminary data it would appear that the so-called desulphurization reaction  $\text{FeS} + \text{CaO} \rightarrow \text{CaS} + \text{FeO}$  may not proceed at all. Dr. R. S. Dean suggested that all of the known facts fitted in with the hypothesis that desulphurization resulted from reduction of  $\text{CaO}$  to metallic calcium, which then entered the metal phase and transported  $\text{CaS}$  to the slag phase. This is consistent with the established fact that strong reducing conditions are necessary for active desulphurization. This reasoning led to the idea that calcium carbide should be a far better desulphurizer than lime, since it reacts with many metals—for example, lead—to give metallic calcium. It would not be expected that an appreciable calcium content would be built up in the metal because of its volatility; hence a dispersion of the carbide through the melt would be necessary for best results.

An examination of the literature showed that an extensive investigation of the use of calcium carbide as a desulphurizer was made by Farrell.<sup>1</sup> Others that have considered the use of carbide are Koppers,<sup>2</sup> Ellis,<sup>3</sup> Davies,<sup>4</sup> and Heimes.<sup>5</sup> Previous investigators have attempted desulphurization by the addition of calcium carbide or a carbide-slag mixture to a crucible or a ladle of molten iron, and in that way have sought to utilize the strong desulphurizing power of the carbide without the aid of an electric furnace. These attempts have resulted in unsatisfactory desulphurization because of ineffective application of the carbide.

Our investigations show that when a small amount of calcium carbide is properly dispersed through molten pig iron containing sulphur a rapid reaction results. Laboratory experiments and foundry tests indicate interesting possibilities for the production of metal containing less than 0.01 per cent S.

#### DESULPHURIZATION WITH ALKALIES

Desulphurization with alkalies has been employed in many foundries for some time, and in the production of wrought iron by the Aston process. It has been occasionally used in steel plants for the treatment of off-casts of pig iron, and in plants where the raw materials carried excessive amounts of sulphur. More recently, however, this method of desulphurization has been modified by H. A. Brassert and Co., and has become a regular step in the smelting of high-sulphur materials in the blast furnace. Economies in furnace operation have resulted from this practice, which was discussed by Colclough,<sup>6</sup> and more recently by Kinney.<sup>7</sup> A résumé of American practice on desulphurization with alkalies was presented recently by Evans.<sup>8</sup> Data in these references have proved helpful in evaluating calcium carbide as a desulphurizer.

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<sup>1</sup> References are at the end of the paper.



## CHEMISTRY OF DESULPHURIZATION WITH CALCIUM CARBIDE

Calcium carbide is a solid at temperatures encountered in the handling of molten pig iron. The melting point of the pure compound is given as approximately  $2300^{\circ}\text{C}$ . The commercial product probably averages 75 to 80 per cent  $\text{CaC}_2$ , and its melting point is somewhat lower. Instead of the conventional liquid-liquid reaction through which final desulphurization is accomplished in the blast furnace or electric furnace, the reaction in this method is probably a solid-liquid reaction with the formation of metallic calcium, as suggested earlier. The sulphur in the metal is eliminated as  $\text{CaS}$ , which, with the excess  $\text{CaC}_2$  and the  $\text{CaO}$  in commercial carbide, forms a dross or crust.

## METHODS OF ADDING CARBIDE

The success of this method of desulphurization is dependent upon the manner in which the carbide is applied or added to the molten iron. The following procedures were investigated, and satisfactory desulphurization was obtained with procedures 1, 4 and 5.

1. A dispersion of the finely ground carbide was produced below the metal surface by immersing a mixture of flux and carbide. Sodium chloride was the most effective of the fluxes tried, besides being relatively inexpensive. A briquet of carbide and salt was placed in an inverted cup holder and forced to the bottom of the metal bath where the salt melted and volatilized,

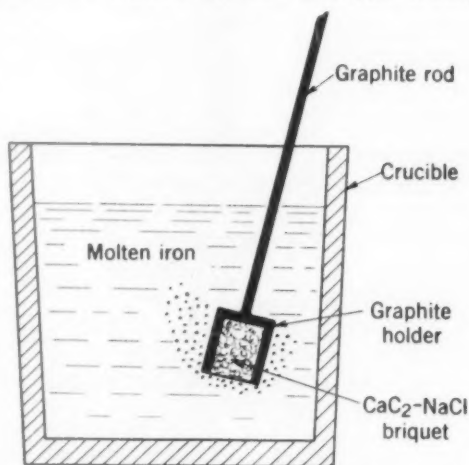


FIG. 1.—METHOD OF ADDING CALCIUM CARBIDE AND SODIUM CHLORIDE.

thereby disintegrating the briquet with the formation of a large surface of carbide to react with the metal. The holder for introducing the salt-carbide briquet is shown in Fig. 1. A device similar in principle has been used by Joseph and associates<sup>9</sup> in the treatment of cast iron with caustic soda.

2. Carbide was added to the hot metal stream in the blast-furnace runner and cupola spout.

3. Carbide or carbide-salt mixture was placed in the bottom of the ladle immediately before the metal was tapped into it.

4. Dispersion of the finely ground carbide was produced by a mechanical unit similar to that shown in Fig. 2. With this type of mechanism the carbide was introduced below the surface of the molten metal through a stationary feed tube and stirred rapidly into the metal bath. The

distributing head was constructed from a graphite electrode, which was easily machined and has comparatively high strength at the temperatures obtaining.

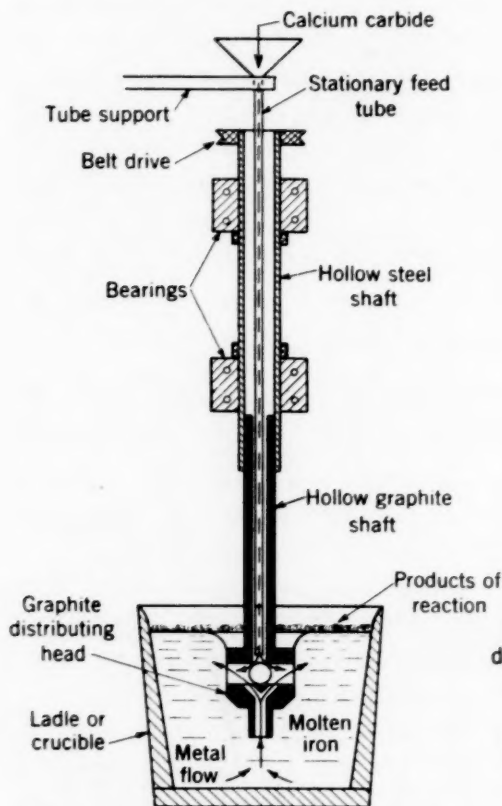


FIG. 2.—INTERNAL FEED-DISPERSION MECHANISM.

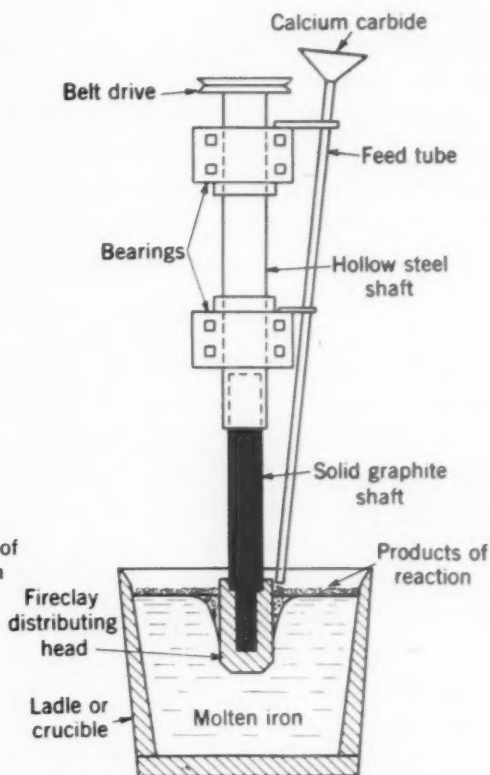


FIG. 3.—EXTERNAL FEED-DISPERSION MECHANISM.

5. Dispersion of the finely ground carbide was produced near the surface of the metal, as shown in Fig. 3.

6. Carbide was added with a slinger of the centrifugal type.

#### CRUCIBLE TESTS WITH CHEMICAL DISPERSERS

Crucible tests with 200-gram to 300-gram charges of metal were made with the high-frequency induction furnace. Finely ground carbide and flux were intimately mixed and pressed into a briquet  $\frac{5}{8}$  in. in diameter and forced below the metal surface, as shown in Fig. 1. After a few minutes the briquet had disintegrated and the reaction had ceased. Comparative tests made in graphite and fire-clay crucibles showed that carbon from the crucible was not essential to the reaction.

Table 1 gives the results obtained with mixtures of carbide and various fluxes. The carbide used for these experiments was the commercial grade containing about 75 per cent  $\text{CaC}_2$ .

## DESULPHURIZATION OF 150-LB. CHARGES OF METAL WITH CARBIDE-SALT MIXTURES

Charges of 150 lb. of cast-iron scrap were melted in an electric arc furnace, and the sulphur content of the metal was increased when necessary by the addition of ferrous sulphide. A mixture of minus 20-mesh carbide and salt was briquetted and applied in the manner employed in the crucible tests. The temperature of the hot metal was measured

TABLE 1.—*Crucible Tests Showing Desulphurization of Pig Iron with Calcium Carbide*

Test No.	Sulphur in Metal, Per Cent		Sulphur Removed, Per Cent	Temperature, Deg. C.	Time of Contact, Min.	Desulphurizer		Kind of Crucible
	Initial	Residual				Material	Percentage of Metal	
1	0.18	0.056	68.9	1450	3	{ CaC <sub>2</sub> CaF <sub>2</sub>	0.5 0.5	Graphite
2	0.16	0.067	58.1	1400	3	{ CaC <sub>2</sub> CaCl <sub>2</sub>	0.5 0.5	Graphite
3	0.16	0.015	90.6	1400	3	{ CaC <sub>2</sub> NaCl	0.5 0.5	Graphite
4	0.16	0.004	97.5	1400	5	{ CaC <sub>2</sub> NaCl	0.5 0.5	Graphite
5	0.16	0.019	88.1	1400	3	{ CaC <sub>2</sub> NaF	0.5 0.5	Graphite
6	0.16	0.007	95.6	1400	5	{ CaC <sub>2</sub> NaF	0.5 0.5	Graphite
7	0.11	0.015	86.4	1400	3	{ CaC <sub>2</sub> NaCl	0.5 1.0	Fire clay
8	0.06	0.012	80.0	1400	3	{ CaC <sub>2</sub> NaCl	0.5 1.0	Fire clay
9	0.06	0.007	88.3	1400	5	{ CaC <sub>2</sub> NaCl	0.5 1.0	Fire clay

with a tungsten-graphite thermocouple immediately before the desulphurizer was added and at the completion of the treatment, and the average for the test was recorded. These temperature measurements show that desulphurization by calcium carbide can be accomplished at temperatures obtaining in the blast-furnace ladle or in the mixer. Data obtained in this series of tests are given in Table 2.

Changes in metal composition during desulphurization with carbide are summarized in Table 3. Manganese and silicon are affected much less by this treatment than by alkali desulphurization, although a small decrease is shown in both elements. An increase is shown in carbon content which may be accounted for by the carbon pickup from contact

with the graphite holder used in applying the carbide. No change in phosphorus content resulted.

#### CRUCIBLE TESTS WITH MECHANICAL DISPERSING UNIT

The results of preliminary crucible tests with the mechanical dispersing unit are recorded in Table 4. A metal charge was melted and preheated to 1400° C. before each test was started, but the change in temperature during the treatment of the metal was not determined. Some drop in temperature always resulted from the introduction of the cold mechanism, and the temperature recorded represents the maximum in each test.

TABLE 2.—*Desulphurization of 150-lb. Charges of Pig Iron*

Test No.	Sulphur in Metal, Per Cent			Sulphur Removed Per Cent	Desulphurizer		Average Temperature of Test, Deg. C.
	Initial	Four-minute Sample	Eight-minute Sample		Material	Percentage of Metal	
61	0.056	0.027	0.022	60.7	{ CaC <sub>2</sub> NaCl	0.67 0.67	1400
63	0.063	0.050	0.025	60.3	{ CaC <sub>2</sub> NaCl	0.5 0.5	1400
65	0.049	0.032	0.021	57.2	{ CaC <sub>2</sub> NaCl	0.5 0.5	1382
70	0.039	0.017	0.015	61.5	{ CaC <sub>2</sub> NaCl	0.5 0.83	1337
71	0.026	0.012	0.012	53.8	{ CaC <sub>2</sub> NaCl	0.33 0.67	1355
56	0.075	0.072	0.073	3.3	NaCl	0.5	1396
57	0.061	0.055	0.052	14.7	CaC <sub>2</sub>	0.5	1436

TABLE 3.—*Changes in Metal Composition during Desulphurization of 150-lb. Charges of Pig Iron*

Test No.	Sulphur		Phosphorus		Manganese		Silicon		Carbon		Average Temperature, Deg. C.
	Before	After	Before	After	Before	After	Before	After	Before	After	
61	0.056	0.022	0.37	0.36	0.65	0.55	1.17	1.13	3.18	4.00	1400
63	0.063	0.025	0.35	0.36	0.64	0.59	1.12	1.14	4.22	4.26	1400
65	0.049	0.021	0.36	0.35	0.63	0.56	1.22	1.21	4.31	4.34	1382
70	0.039	0.015	0.36	0.36	0.58	0.57	1.27	1.24	4.10	4.24	1337
71	0.026	0.012	0.36	0.34	0.55	0.62	1.28	1.23	4.31	4.34	1355

Employing the laboratory mechanism shown in Fig. 2, the time required for the addition of an equivalent of 10 lb. of carbide per ton of metal was between one and two minutes. Table 4, which shows the

TABLE 4.—*Crucible Tests with the Mechanical Dispersing Unit*

Test No.	Sulphur in Metal, Per Cent			Sulphur Removed, Per Cent	Crucible	CaC <sub>2</sub> Used		Weight of Metal Charge, Grams
	Initial	Two-minute Sample	Final from Ingot			Size, Mesh	Amount, Lb. per Net Ton	
126	0.097	0.007	0.007	92.7	Graphite	-48 + 180	10	1600
127	0.083	0.012	0.009	89.2	Magnesia	-48 + 180	10	1600
132	0.096	0.027	0.019	80.2	Fire clay	-48 + 180	10	1600

results of samples obtained 2 min. after completion of the carbide addition compared with final ingot samples, demonstrates the speed with which hot metal and fine carbide without the addition of fluxes react when a suitable mixing method is applied. The tests conducted in graphite and magnesia crucibles resulted in slightly higher carbide efficiencies than when a fire-clay crucible was used. However, it was shown by later tests that metal with the same low sulphur content may be produced with a small increase in the carbide addition.

#### EFFECT OF PARTICLE SIZE OF CARBIDE ON DESULPHURIZATION

A series of tests was made with closely sized calcium carbide, to determine the effect of particle size on desulphurization. The equivalent

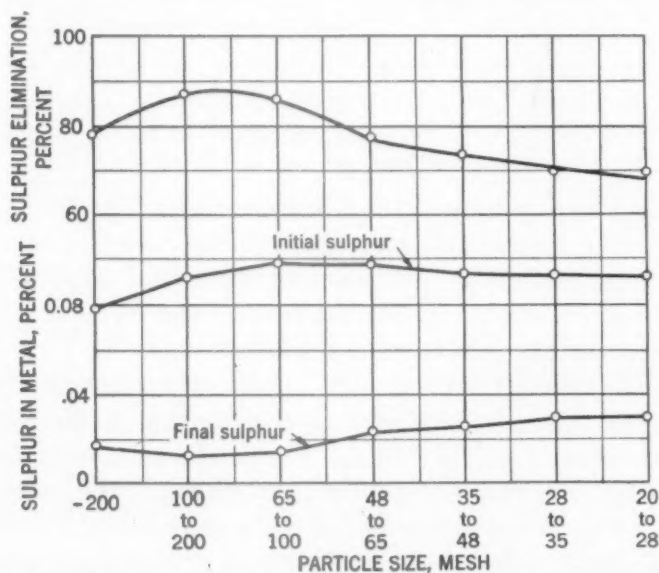


FIG. 4.—EFFECT OF PARTICLE SIZE OF CARBIDE ON DESULPHURIZATION.

of 10 lb. of carbide per ton of metal was added to the metal with the internal feed-distributing head. A metal charge of approximately 8 lb. was melted and preheated to 1400° C. before each test was started. Fig. 4 shows the effect of particle size on desulphurization when the weight of carbide, the amount of agitation, and the weight of metal and



its temperature were approximately the same. These data indicate a maximum carbide efficiency for the minus 65 plus 100-mesh size. Test 1 shows that too fine grinding results in a decreased efficiency, owing probably to the loss of carbide during grinding by reaction with oxygen or moisture in the atmosphere. Theoretically the smaller particles should be more efficient because of greater opportunity for contact between carbide and molten metal.

#### SULPHUR REVERSION AFTER TREATMENT WITH CARBIDE

Return of sulphur from the slag to the metal after desulphurization occurs in the treatment with alkali unless the slag and metal are separated at the proper time. This resulphurization is attributed mainly to the silica taken up by the basic slag through oxidation of part of the silicon

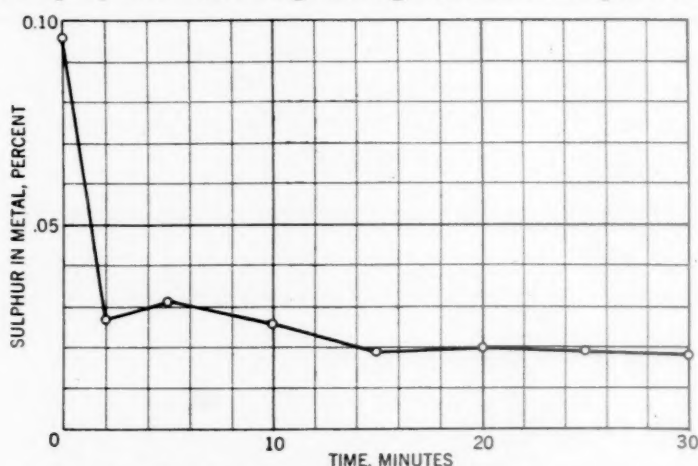


FIG. 5.—EFFECT OF TIME ON REVERSION OF SULPHUR.

in the metal and to corrosion of the silicate lining of the ladle. The silica combines with the alkali oxide, and the desulphurizing power of the slag is reduced proportionately. It is conceivable that some of the resulphurization may be caused by an increase in the ferrous oxide content of the slag as a result of atmospheric oxidation.

Calcium sulphide and calcium oxide, unlike the corresponding sodium compounds, are solids at temperatures occurring in desulphurization, and show little or no tendency to react with the refractory lining of the crucible or ladle. There is less oxidation of silicon in the metal, the crust formed during desulphurization remains strongly basic, and no sulphur returns to the metal. Fig. 5 shows the effect of holding a desulphurized bath of metal for 30 minutes in contact with the high-sulphur crust.

#### RESULTS OF TESTS AT STEEL PLANTS

Large-scale desulphurization tests were conducted at three steel plants before the mechanical dispersion unit was developed. The results of these tests were disappointing when considered on the basis

of sulphur elimination. Important observations were made, however, on methods of adding the carbide to large quantities of hot metal. Failure to obtain more satisfactory desulphurization was due to insufficient contact between the carbide and hot metal by the methods employed and to the size of the carbide, which was too coarse in most instances.

Results of the plant tests, summarized in Table 5, show that the most efficient use of carbide is attained when the desulphurizer is placed in the bottom of the ladle immediately before the metal is tapped.

TABLE 5.—*Tests Made at Steel Plants*

Test No.	Sulphur in Metal, Per Cent		Sulphur Elimination, Per Cent	Carbide Addition		Weight of Metal Treated, Tons	Temperature of Metal, Deg. F.	Method of Adding Carbide
	Before Treatment	After Treatment		Pounds per Ton of Metal	Commercial Size, <sup>a</sup> Designation			
1	0.024	0.019	20.8	10	Dust	5	2460	To metal stream in runner.
2	0.027	0.019	29.6	10	Dust	5	2470	In bottom of ladle.
3	0.025	0.025	None	10	Gran	5	2475	Half to ladle; half to runner.
4	0.041	0.040	2.5	10	Gran	5	2440	In bottom of ladle.
5	0.024	0.020	16.6	10	Dust	25	2350	To ladle in 12-lb. paper bags as metal was tapped.
6	0.039	0.036	7.7	10	14ND	25	2280	To ladle in 12-lb. paper bags as metal was tapped.
7	0.104	0.072	30.7	14	Gran	12	2710	In ladle in 7-ft. length of 8-inch iron pipe.
8	0.039	0.025	35.9	10	Dust	25		In bottom of ladle mixed with 20 per cent NaCl.
9 <sup>b</sup>	0.045	0.028	37.8	10	Dust	3	2400	In bottom of ladle with equal weight of NaCl.
10 <sup>b</sup>	0.050	0.038	24.0	10	Dust	9		In bottom of ladle with equal weight of NaCl.
11 <sup>c</sup>	0.095	0.045	52.6	11	Rice	13.7		In bottom of ladle with equal weight of NaCl.

<sup>a</sup> Approximate size of commercial carbide: Gran is largely minus 20-mesh with some minus 5 plus 20-mesh material; 14ND, minus 10 plus 32-mesh; Dust, 50 per cent minus 20 plus 48-mesh, 50 per cent minus 48-mesh; Rice, minus 8 plus 10-mesh.

<sup>b</sup> Tests were conducted under supervision of E. F. Wilson, Metallurgy of Steel Section, Bureau of Mines.

<sup>c</sup> Test was conducted by staff of A. M. Byers Co.

## FOUNDRY TESTS

A mechanical dispersion unit for treating 1-ton charges of hot metal was developed in cooperation with the St. Paul Foundry Co., St. Paul, Minn. This unit is essentially the same in principle as the laboratory unit and is illustrated in Fig. 6. Details of the two types of distributing heads found suitable for the treatment of large amounts of hot metal are shown diagrammatically in Figs. 7 and 8. Satisfactory mixing of the carbide and metal was obtained with the distributing head operating at a speed of approximately 600 r.p.m. Results of the foundry tests are given in Table 6. A maximum sulphur extraction of 93.5 per cent

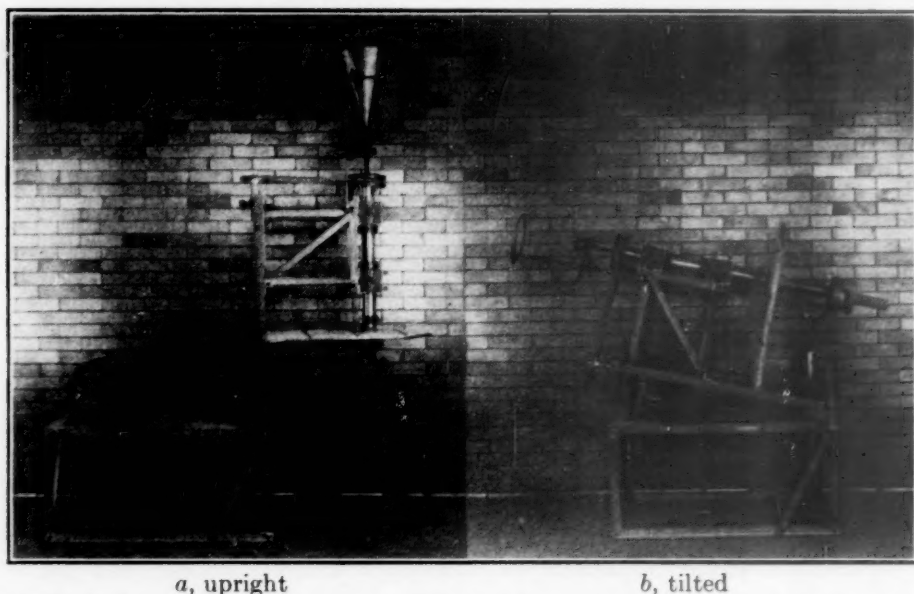


FIG. 6.—FOUNDRY DISPERSION UNIT FOR ADDING CALCIUM CARBIDE TO MOLTEN CAST IRON.

was obtained in test 6, in which the sulphur content of the metal was reduced from 0.092 to 0.006 per cent in a treatment period of 7.75 min. Metal containing less than 0.01 per cent S apparently can be consistently produced by this method.

The internal feed-distributing head shown in Fig. 7 was used in tests 1 to 8, and the external feed-distributing head in Fig. 8 was used in tests 9 and 10. Sulphur extraction with an equivalent weight and size of carbide was nearly the same for both methods of application when the best test was considered in each case. The slightly better efficiency obtained with the internal feed distributor would be offset by its more complicated design.

The depth to which the internal feed-distributing head was immersed in the metal bath has a marked effect on the efficiency of the carbide

TABLE 6.—*Tests Made at Foundry*

Test No.	Sulphur in Metal, Per Cent				Sulphur Elimination, Per Cent	Carbide Addition		Treatment Period, Min.	Immersion, Top of Distributing Head below Metal Surface, In.
	Before Treatment	After Treatment				Pounds per Ton	Size, Mesh		
		Top of Ladle	Bottom of Ladle	Dross Metal					
1	0.100	0.031	0.032	0.011	68.5	10	-48 + 200	4	1
2	0.086	0.031	0.031	0.007	64.0	10	-48 + 200	4	1.5
3	0.095	0.084	0.079	No metal	14.2	5	-48 + 200	2.5	3
4	0.094	0.075	0.075	0.052	20.2	10	-48 + 200	4.5	3
5	0.102	0.017	0.011	0.004	86.3	12.25	-48 + 200	6	1
6	0.092	0.006	0.006	0.006	93.5	15	-48	7.75	1
7	0.083	0.029	0.029	0.006	65.1	11	-20 degassed	6.3	1
8	0.085	0.039	0.042	0.036	52.4	11	-20 regular	8	1
9	0.090	0.034	0.033	No metal	62.8	15	-48	6	1
10	0.089	0.015	0.013	0.008	84.3	15	-48	6.5	1

addition. Tests 3 and 4 indicate that when the immersion was 3 in. below the stationary surface of the metal in the ladle the mixing of the carbide and the metal was less effective than when the immersion was 1 in. The mechanism of the reaction appears to require rapid stirring of the carbide into the metal at the point of application. The effect of depth of immersion was not determined for the external feed distributor, but it is obvious that there would be an optimum depth.

When finely ground carbide is heated an appreciable amount of acetylene is released. This acetylene is assumed to be adsorbed on the carbide particles and to have formed during the screening and grinding operations as a result of the reaction of the carbide with moisture in the atmosphere. Tests 7 and 8 were made to determine the effect of this adsorbed acetylene on the efficiency of the treatment with carbide. Some of the minus 20-mesh carbide, which had been heated to drive off the adsorbed acetylene, was compared with an equivalent amount of unheated minus 20-mesh material. A slight advantage was indicated for the degassed material from the results of these two tests, but the effect should be verified by further tests, since undetermined variables may have been the cause of some of this difference.

It is of particular significance to note the very low sulphur content of the metal occluded in the dross in most cases. In test 6, in which practically complete desulphurization was obtained, the sulphur content of the metal in the ladle was the same as that of the dross metal. The sulphur content of the dross metal was much lower than that of the ladle metal in most of the tests. The reaction closely approached equilibrium only in test 6. The treatment period was cut short to avoid excessive cooling of the metal, which, after the test, was poured into

soft-iron castings. A longer agitation period should result in more consistent desulphurization.

An investigation of the effect of desulphurization with carbide on the physical properties and microstructure of the treated iron would be interesting but was not made, since the main objective of the investigation was to determine the lower limit of desulphurization that could be expected from this type of treatment. However, an increase was

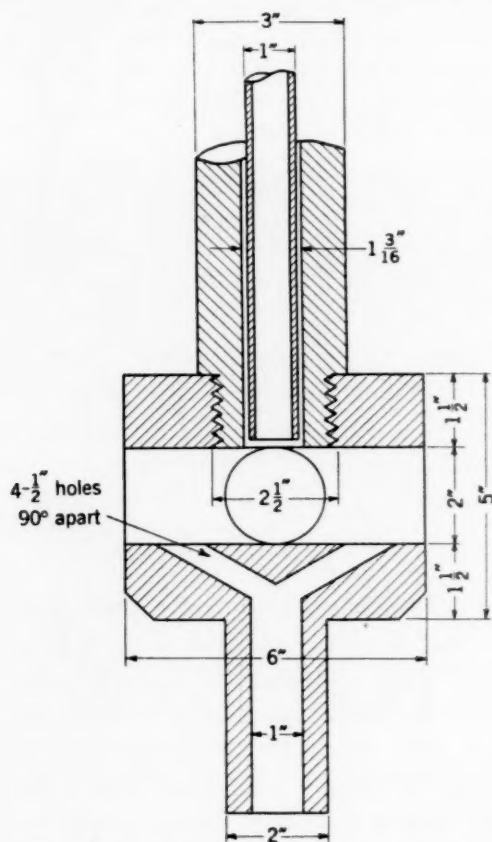


FIG. 7.—SECTION OF INTERNAL FEED-DISTRIBUTING HEAD.

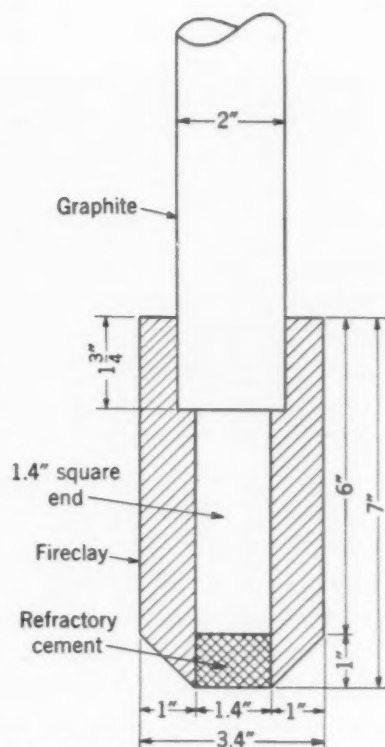


FIG. 8.—SECTION OF EXTERNAL FEED-DISTRIBUTING HEAD.

observed in the machinability of the iron after complete desulphurization, when the samples were drilled for analysis.

Changes in the composition of the metal during treatment with carbide are shown in Table 7. The manganese and phosphorus in the metal were unaffected within the limits of sampling and chemical analysis. Carbon showed greater fluctuation but no regular trend, except in the cross metal, where there was a decrease.

Silicon showed a consistent increase when the carbide was applied with the internal feed-distributing head, the maximum being 10.1 per cent of the total silicon present. Application of the carbide with the external feed distributor resulted in a small decrease in silicon content.



# EFFECT OF CARBIDE ADDITIONS ON LADLE REFRACTORIES

The foundry tests in which calcium carbide was used without the addition of fluxes indicated that the fluxing action of the carbide on the fire-clay lining of the ladle would apparently be slight in this type of desulphurization. The products of the reaction formed a dross or crust on top of the metal bath and no fluid slag was produced during the operation. If carbide-salt mixtures were used there would be some opportunity for the alkali to react with the lining to form sodium silicate, but the corrosion would be much less than with the soda ash or caustic soda treatment. The refractory costs for desulphurization with carbide therefore should be correspondingly less.

## APPLICATION OF PROCESS

The extent to which calcium carbide may be used as an auxiliary desulphurizer will depend on the ultimate cost of the treatment of large amounts of metal and on the demand for metal containing less than 0.02 per cent S. Desulphurization with carbide appears to offer some advantage over the use of alkalis in the production of metal with an extremely low sulphur content. As a sulphur content of 0.02 per cent is approached the efficiency of the alkalis decreases rapidly, while the carbide continues to be effective. Metal containing 0.01 per cent or less of sulphur can be

TABLE 7.—Changes in Composition of Foundry Iron during Desulphurization with Calcium Carbide  
Per Cent

Sulphur				Carbon				Silicon				Manganese				Phosphorus				
Test No.	Before Treatment	After Treatment			Before Treatment	After Treatment			Before Treatment	After Treatment			Before Treatment	After Treatment			Before Treatment	After Treatment		
		Top of Ladle	Bottom of Ladle	Dross of Metal		Top of Ladle	Bottom of Ladle	Dross of Metal		Top of Ladle	Bottom of Ladle	Dross of Metal		Top of Ladle	Bottom of Ladle	Dross of Metal		Top of Ladle	Bottom of Ladle	Dross of Metal
1	0.100	0.031	0.032	0.011	3.58	3.63	3.60		1.82	1.86	1.94		0.65	0.63	0.65		0.31	0.30		
5	0.102	0.017	0.011	0.004	3.52	3.57	3.45	1.84	1.69	1.88			0.56	0.55	0.55	0.38	0.38	0.37		
6	0.092	0.006	0.006	0.006	3.69	3.69	3.68		1.46	1.45	1.49		0.59	0.58	0.58	0.21	0.21	0.20		
9	0.090	0.034	0.033		3.60	3.62	3.57		1.86	1.74	1.72		0.58	0.56	0.54	0.28	0.27	0.27		
10	0.089	0.015	0.013	0.008	3.54	3.53	3.41	1.67	1.71	1.69			0.64	0.64	0.60	0.23	0.22	0.23		

produced at a cost that does not appear to be excessive for this type of metal.

Desulphurization outside the blast furnace is a possible method of producing low-sulphur, low-silicon basic iron, as pointed out by Joseph and associates (see ref. 9, p. 329), as follows:

Moreover, the production of basic iron containing about one-half of the normal amount of silicon and 0.02 per cent S or under is receiving considerable discussion. Since the high temperatures necessary to eliminate sulphur in the blast furnace are diametrically opposed to the production of low-silicon iron, desulphurization outside the blast furnace affords a possible means of producing basic iron low in both silicon and sulphur.

A part of the cost of the carbide treatment can be offset in some instances by operating the blast furnace on a more acid slag, which would result in a lowering of the coke consumption, an increase in production of pig iron, and in a smoother operating furnace.

#### ACKNOWLEDGMENTS

This investigation was undertaken at the suggestion of Dr. R. S. Dean, chief engineer, Metallurgical Division, Bureau of Mines, and carried out under his supervision. The authors wish to acknowledge the assistance given by members of the Metallurgy of Steel Section at the Pittsburgh station of the Bureau of Mines, especially by E. F. Wilson, who took a major part in the plant tests conducted in the Pittsburgh district.

It is not possible in the space allotted to mention individually all outside the Bureau who have contributed to this investigation. Tests were made at the following steel plants in the Pittsburgh district: A. M. Byers Co., Ambridge, Pa.; Jones & Laughlin Steel Co., Aliquippa, Pa.; and Pittsburgh Steel Co., Monessen, Pa. The calcium carbide was furnished through F. Pruyn, Jr., of the National Carbide Co., and R. C. Good, of the Union Carbide and Carbon Company.

The authors wish to acknowledge especially the assistance and cooperation of F. S. Power, R. P. Wassberg, and others of the St. Paul Foundry Co., at which plant the mechanical dispersion method of treatment was developed. F. Pruyn Jr., of the National Carbide Co., and J. A. Schindler, of the Air Reduction Sales Co., also assisted with the foundry tests.

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## DISCUSSION

(C. E. Sims presiding)

C. L. WAGGONER, \* Chicago, Ill.—I notice that when the carbide addition is made to the metal runner, ladle, etc., in a manner that might be described as crude (particularly in Table 5), the sulphur in the metal, after treatment, is about the same as would be expected when additions of soda ash are made in this manner. The question is: Do the authors attribute the high percentage of sulphur removal indicated by other tables to the efficiency of the carbide itself or to the improved method of adding this material?

E. P. BARRETT (author's reply).—The authors have demonstrated the importance of the method of adding granular (minus 48-mesh) calcium carbide to molten cast iron in the desulphurization of cast iron with calcium carbide. The method of adding calcium carbide to molten cast iron being agitated by a mechanical stirrer is superior to the five other methods used in the investigation.

In Table 5, data are shown from 11 tests in which calcium carbide was added to molten cast iron by a number of methods other than mechanical agitation. The average amount of sulphur before treatment was 0.0466 per cent, which was reduced to only 0.0333 per cent by the addition of an equivalent of 10 lb. of calcium carbide per ton of metal. This represents the removal of 28.8 per cent of the sulphur present before treatment.

The method of adding calcium carbide to molten cast iron being agitated by a mechanical stirrer was used on cast irons containing as little as 0.023 per cent and as much as 0.123 per cent of sulphur.

Data from 22 tests on 6 to 10 lb. of cast iron heated to 1400°C. in an induction furnace have been arranged in two groups: group 1 (0.070 to 0.123 per cent S) in Table 8 and group 2 (0.023 to 0.053 per cent S) in Table 9. The average percentage of sulphur in the cast iron before treatment in 16 tests shown in Table 8 was 0.0945 per cent, which was reduced to an average of 0.0194 per cent by stirring in calcium carbide equivalent to 10 lb. per ton of cast iron in an average period of 4 min. from the beginning of the carbide addition to the sampling of the metal 2 min. after the carbide addition was completed. The average amount of sulphur in the cast iron before treatment, in the six tests shown in Table 9, was 0.0345 per cent, which was reduced to an average of 0.0075 per cent by stirring in calcium carbide equivalent to 10 lb. per ton of cast iron in an average of 4 min. from the beginning of the carbide addition to the sampling of the metal 2 min. after the carbide addition was completed. In test 164 in Table 9, minus 28-mesh calcium carbide equivalent to 5 lb. per ton of cast iron reduced the sulphur from 0.023 to 0.009 per cent.

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\* Plant Manager, Interlake Iron Corporation.

*Effect of Amount of Iron Treated.*—The data from six tests on 2000 lb. of cast iron in a foundry ladle are shown in Table 10. The sulphur in the cast iron averaged 0.0933 per cent, which was reduced to an average of 0.0225 per cent by stirring in calcium carbide equivalent to 12.9 lb. per ton of metal in an average of 5.7 min. from

TABLE 8.—*Tests on High-sulphur Metal*<sup>a</sup>  
(0.07 to 0.123 Per Cent S)

Test No.	Sulphur, Per Cent		Calcium Carbide		Feed Tube	Minutes from Start of CaC <sub>2</sub> Addition
	Before Treatment	After Treatment	Equivalent Lb. per Ton	Size, Mesh		
149	0.106	0.029	10	— 48 + 65	Internal	5
150	0.097	0.022	10	— 48 + 65	Internal	4½
151	0.070	0.008	10	— 65 + 100	Internal	4½
152	0.092	0.012	10	— 100 + 200	Internal	4½
155	0.093	0.026	10	— 35 + 48	Internal	4
158	0.092	0.028	10	— 28 + 35	Internal	4
160	0.096	0.028	10	— 20 + 28	Internal	4
162	0.076	0.015	10	— 20 + 28	Internal	4
183	0.085	0.004	10	— 48 + 200	Internal	4
187	0.078	0.017	10	— 200	Internal	3½
195	0.100	0.023	10	— 48 + 200	External	4
197	0.100	0.019	10	— 48 + 200	External	3¼
198	0.088	0.019	10	— 48 + 200	External	3¼
200	0.123	0.019	10	— 65 + 100	Internal	4
201	0.106	0.028	10	— 48 + 200	External	4
202	0.113	0.013	10	— 48 + 200	External	4
Average.....	0.0945	0.0194	10			4

<sup>a</sup> Average S removed per pound of carbide, 0.0075 per cent; average percentage of total sulphur removed, 79.47.

TABLE 9.—*Tests on Low-sulphur Metal*<sup>a</sup>  
(0.023 to 0.053 Per Cent S)

Test No.	Sulphur		Calcium Carbide		Minutes from start of CaC <sub>2</sub> Addition
	Before Treatment	After Treatment	Equivalent, Lb. per Ton	Size, Mesh	
153	0.053	0.007	10	— 200	5
154	0.034	0.010	10	— 100 + 200	3½
156	0.032	0.007	10	— 28 + 35	4
157	0.025	0.004	10	— 20 + 28	4
164	0.023	0.009	5	— 28	4
185	0.040	0.008	10	— 200	4
Average.....	0.0345	0.0075	9		4

<sup>a</sup> Average S removed per pound of carbide, approximately 0.003 per cent. Average percentage of total sulphur removed, 78.26.



the beginning of the carbide addition to the sampling of the metal 2 min. after the carbide addition was completed. The tests shown in Table 10 were made on 200 times as much iron as those shown in Table 8, yet the average reduction in sulphur content of the metal is nearly the same.

In the 16 tests shown in Table 8, the sulphur removed per pound of carbide per ton of iron ranged from 0.0061 to 0.0140 per cent, with an average of 0.0075 per cent. The average amount of sulphur removed in six tests in the foundry on 1-ton ladles of cast iron (Table 10) was 0.0055 per cent. One reason for the lower average sulphur removal in the foundry is that the stirrer was not as flexible and the amount of agitation was not as great as in the laboratory tests on 6 to 10 lb. of iron.

T. L. JOSEPH,\* Minneapolis, Minn.—How does the theoretical efficiency of calcium carbide as a desulphurizer compare with that of soda ash?

TABLE 10.—*Tests on 1-ton Ladles of High-sulphur Metal in a Foundry<sup>a</sup>*

Test No.	Sulphur		Calcium Carbide		Minutes from Start of CaC <sub>2</sub> Addition
	Before Treatment	After Treatment	Weight, Lb.	Size, Mesh	
170	0.100	0.032	10	-48 + 200	4
180	0.086	0.031	10	-48 + 200	4
193	0.102	0.017	12.3	-48 + 200	6
203	0.092	0.006	15	-48	7 $\frac{3}{4}$
210	0.090	0.015	15	-48	6 $\frac{1}{2}$
215 <sup>b</sup>	0.090	0.034	15	-48	6
Average.....	0.0933	0.0225	12.9		5.7

<sup>a</sup> Average S removed per pound of carbide, about 0.0055 per cent. Average percentage of total sulphur removed, 75.88.

<sup>b</sup> Test 215 was stirred with the 3 $\frac{1}{2}$  by 3 $\frac{1}{2}$  by 7-in. refractory head used in test 210. This head was formed by hand from A.P. green superplastic firebrick.

E. P. BARRETT (author's reply).—Theoretically, 2 lb. of 100 per cent CaC<sub>2</sub> will combine with 1 lb. of sulphur. Because commercial calcium carbide is about 75 per cent CaC<sub>2</sub>, 2.67 lb. will be required to combine with 1 lb. of sulphur. Soda ash is nearly 100 per cent Na<sub>2</sub>CO<sub>3</sub>, and 3 lb. will be required to combine with 1 lb. of sulphur. On this basis, the theoretical efficiency of commercial calcium carbide is 1.13 times that of soda ash.

The relative actual efficiencies of commercial calcium carbide and soda ash are shown in Table 11. The data relative to the efficiency of soda ash are from Fig. 5 by Evans (ref. 8). These data indicate that commercial calcium carbide is 1.5 times as efficient as soda ash.

R. A. LINDGREN,† South Chicago, Ill.—How do the economics of desulphurizing with calcium carbide compare with soda ash?

E. P. BARRETT (author's reply).—Exact costs cannot be determined from the small-scale tests made in this investigation. A fair approximate cost may be made, however. For convenience, the cost will be considered in three groups:

\* Professor of Metallurgy, University of Minnesota.

† Superintendent, Blast Furnace Dept., Wisconsin Steel Works.



1. *Reagent*.—Calcium carbide, minus 48-mesh, is priced at about 5¢ per pound. With properly designed apparatus, 1 lb. of minus 48-mesh calcium carbide should remove 0.0075 to 0.01 per cent S per ton of metal treated. The cost of reagent probably represents from 60 to 75 per cent of the total cost of treatment.

2. *Stirrer*.—The stirrer is the heart of this process. It should be constructed and mounted carefully so that the position of the refractory head may readily be moved horizontally and vertically and be capable of wide variation in speed of rotation. The greater part of the cost will be for the variable-speed motor. The size of the motor depends on the scale of operation.

Inasmuch as a hand-formed refractory head  $3\frac{1}{2}$  by  $3\frac{1}{2}$  by 7 in. was satisfactory in the tests on 2000 lb. of metal in the foundry, no difficulty should be experienced in obtaining refractory heads from the industry. The cost of refractory heads represents the greater part of the maintenance cost of the stirrer.

TABLE 11.—*Relative Efficiencies of Commercial Calcium Carbide and Soda Ash*

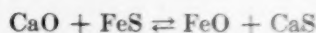
Sulphur Range, Per Cent	Average Sulphur, Per Cent			Reagent (10 Lb. per Ton of Metal)
	Before Treatment	After Treatment	Removed by 1 Lb. of Reagent	
0.07–0.100	0.0850	0.0360	0.00490	Na <sub>2</sub> CO <sub>3</sub>
0.07–0.123	0.0945	0.0194	0.00750	CaC <sub>2</sub>
0.02–0.060	0.0400	0.0204	0.00196	Na <sub>2</sub> CO <sub>3</sub>
0.023–0.053	0.0345	0.0075	0.00300	CaC <sub>2</sub>

3. *Ladle*.—A special ladle is recommended, since there must not be a layer of slag on the surface of the metal when the calcium carbide is added.

When calcium carbide has been stirred into the metal, a noncohesive mass of unused carbide, lime, calcium sulphide, perhaps some calcium sulphate with kish, and some iron shot floats on top of the metal. A teapot-type ladle would be ideal for separating the treated iron from such a mass, which could be removed from the ladle by turning it bottom side up. If a teapot-type ladle is not available, some other type of skimming may be employed.

D. E. BABCOCK, \* Pittsburgh, Pa.—The work presented in this paper is certainly of very real value so far as the future of desulphurization studies and applications are concerned. Efficiencies of desulphurization of the order herein contained are highly attractive if attainable on larger volumes of metal.

Mention was made by the authors of the nature of the mechanism of desulphurization and of their doubt that the reaction



had anything to do with it. The writer would like to point out that the authors have to all practical purposes used this explanation to account for desulphurizing power (p. 94). The possibility of the reaction of reduced metallic calcium acting as the desulphurizer was certainly a more remote possibility from thermodynamic reasons than the one that they have rejected.

The writer does not entirely subscribe to the mechanisms previously suggested either, but suitable explanations for the desulphurization of iron based on the relative

\* Industrial Fellow, Mellon Institute of Industrial Research.

ionic activity of calcium and the Donnan equilibrium effects have not been forthcoming, although they offer the most satisfactory approach to this problem. The reaction herein involved was one of a distinctly heterogeneous nature, involving mainly the solid-liquid interchange reactions.

Our experience with these tests seemed to indicate that desulphurization in the larger tonnages could be raised to high efficiencies only if the ratio of slag contact area to metal volume was a maximum, and the extractions carried out in cascade arrangement rather than an operation.

This method of desulphurization, and incidentally deoxidation as well, should prove useful in commercial induction furnaces of rather large tonnages.

C. E. WOOD, E. P. BARRETT AND W. F. HOLBROOK (authors' reply).—Dr. Babcock has stressed a very important factor affecting the efficient utilization of calcium carbide as a desulphurizer of pig iron. The results of our experiments with various methods of adding calcium carbide to molten pig iron indicate that a large surface of the reagent must be in contact with the metal if good desulphurization is to be obtained. The effect of surface of the calcium carbide on the percentage of sulphur elimination is shown in Fig. 4. The percentage elimination of sulphur increased as the particle size of the carbide decreased from  $-20+48$  mesh to  $-100+200$  mesh. The efficiency of the minus 200-mesh carbide was less than that of the  $-100+200$ -mesh carbide, probably owing to a lower calcium carbide content in consequence of its reaction with oxygen and moisture in the air during grinding and screening.

The calcium carbide must be added to the molten pig iron by a method by which the large surface of the carbide particles is quickly brought into contact with the metal. Minus 48-mesh carbide appears to be a suitable particle size. The data in Tables 8, 9 and 10 show that calcium carbide mechanically stirred into molten pig iron removed an average of 75 to 80 per cent of the sulphur in 4 to 6 min. When calcium carbide was poured or shoveled onto a stream of molten pig iron in a runner, the carbide floated quietly on top of the metal and was agitated only slightly when it entered the ladle. Only 20 per cent of the sulphur was removed by this treatment.

If a cascade arrangement will produce rapid and intimate contact between the metal and nearly all of the surface of the minus 48-mesh particles of calcium carbide, it will simplify the treatment of larger tonnages. An important factor in considering such an arrangement is that calcium carbide is a solid at the temperatures encountered in the handling of molten pig iron. When calcium carbide is stirred into the molten metal, a noncohesive mass of unused carbide, lime, calcium sulphide, perhaps some calcium sulphate mixed with kish, and some iron shot floats on top of the metal. This mass should not be confused with a liquid slag such as is obtained when soda ash is added to molten pig iron.

## Reduction of Iron Ores under Pressure by Carbon Monoxide\*

BY MICHAEL TENENBAUM† AND T. L. JOSEPH,‡ MEMBER A.I.M.E.

(Chicago Meeting, October 1939)

IN a previous investigation<sup>1</sup> the authors studied the effect of pressure on the reduction of iron ores by hydrogen. With hydrogen as a reducing agent, the rate of reduction was increased substantially by increasing the pressure from 1 to 2 atmospheres. The results with hydrogen prompted the present study of the effect of pressure on reduction with carbon monoxide and with mixtures of carbon monoxide and nitrogen.

### FEATURES OF REDUCTION PROCESS

The gas stream in the lower part of the blast furnace always contains sufficient concentrations of reducing gases to complete reduction provided sufficient time is allowed for the reaction to proceed. Reducing gases react immediately with the iron oxide on the surface of lumps of ore. However, as the unreduced surface recedes from the easily accessible exterior of the lump, the reaction proceeds by virtue of the diffusion of the gases into and out of individual pieces.

The rate of diffusion of gases, which undoubtedly plays an important role in the reduction of iron ores, depends on several factors, most important of which are: (1) molecular weight or density, (2) pressure, (3) temperature, (4) concentration gradient. Thus, the rate of reduction of a lump of iron ore at any temperature will depend not only on the specific reaction rate but also upon: (1) available surface of unreduced iron oxide, (2) rate of diffusion of the reducing gas to the reacting surface, (3) rate of effusion of the gaseous products of the reaction from the reacting surface, (4) adsorption of the gases on the reacting surface.

The various features of the reduction process were discussed in previous work and need not be reviewed. However, in order to explain

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\* Assistance in the preparation of the cubical specimens used in this investigation was furnished by the personnel of Works Progress Administration Official Project No. 665-71-3-69; Sub-Project No. 245. Manuscript received at the office of the Institute Sept. 7, 1939. Issued as T.P. 1134 in METALS TECHNOLOGY, December 1939.

† Teaching Assistant, Department of Metallurgy, University of Minnesota, Minneapolis, Minn.

‡ Professor of Metallurgy, University of Minnesota.

<sup>1</sup> References are at the end of the paper.

observed differences in the pressure-reduction characteristics of hydrogen and carbon monoxide, the function of adsorbed films in gas-solid reactions is reviewed in the latter part of this paper.

### EXPERIMENTAL WORK

As in previous work, reduction tests were carried out at pressures of either one or two atmospheres on cubical specimens of ore. All cubes were cut from one large lump of limonitic iron ore to ensure similar physical and chemical properties. Specimens were first dehydrated at 500° C., and with the exception of one series of tests consisted of  $\frac{9}{16}$ -in. cubes. Only cubes of approximately the same porosity were used in reduction tests, thus eliminating a more important physical variable.

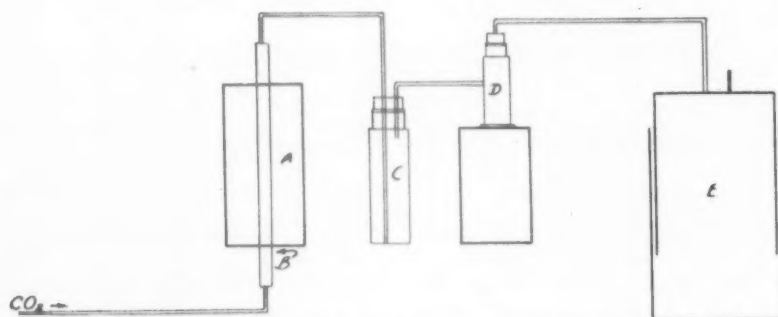


FIG. 1.—DIAGRAMMATIC SKETCH OF APPARATUS FOR PREPARING CARBON MONOXIDE.  
A. Heating furnace. D. Ascarite absorbing tower.  
B. Charcoal-filled iron tube. E. Gas holder.  
C. KOH absorbing tower.

*Preparation of Carbon Monoxide.*—The carbon monoxide was prepared by passing carbon dioxide through a vertical column of hot charcoal maintained at 1025° C. As shown in Fig. 1, any remaining carbon dioxide was removed by potassium hydroxide and ascarite before the gas was collected in a holder.

*Reduction Apparatus and Procedure.*—The method used in determining the rate of reduction with carbon monoxide was essentially the same as that employed for reduction with hydrogen. As the gas was stored over water, it was pumped through a dehydrating tower to remove entrained vapor. Carbon dioxide in the stored gas was eliminated by passing the gas over hot charcoal and then through a tower of ascarite. As shown in Fig. 2, the purified carbon monoxide was then passed over the heated cube of iron ore. The carbon dioxide formed by reduction was collected in alternate towers of ascarite, which were weighed at 10-min. intervals.

The rate of flow of gases was maintained at 600 c.c. per minute. Pressures were measured by means of a large mercury manometer. Special wire clamps were fastened to both ends of the horizontal reduction

tube, to keep the rubber stoppers in place. With the exception of the first two minutes of each reduction, the entire system was kept closed and the pure carbon dioxide gas recirculated by a pump within the circuit.

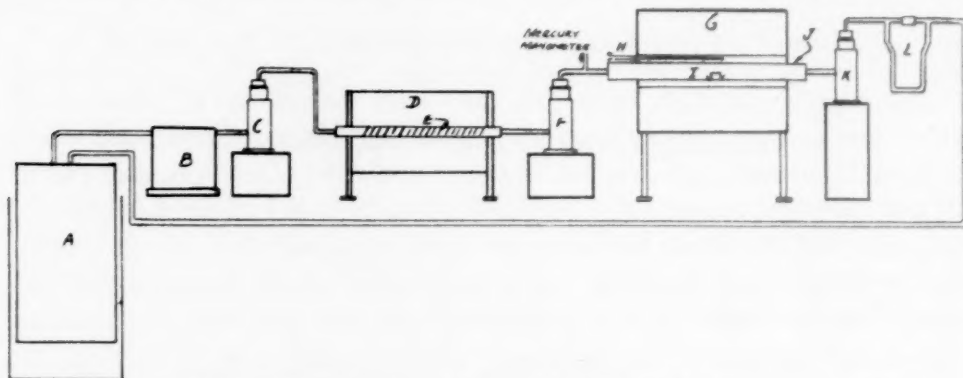
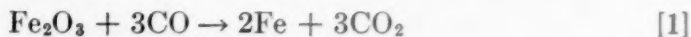


FIG. 2.—DIAGRAMMATIC SKETCH OF REDUCTION APPARATUS.

- |                        |                                      |                      |
|------------------------|--------------------------------------|----------------------|
| A. Gas holder.         | F. CO <sub>2</sub> absorption tower. | J. Vitreosil tube.   |
| B. Pump.               | G. Reduction furnace.                | K. Absorption tower. |
| C. Drying bottle.      | H. Thermocouple.                     | L. Flowmeter.        |
| D. Preheating furnace. | I. Cube and Nichrome screen boat.    |                      |
| E. Charcoal.           |                                      |                      |

#### CARBON DEPOSITION WITH PURE CARBON MONOXIDE

In the presence of iron ore at elevated temperatures, carbon monoxide may react in one of two ways. First, it may deoxidize the ore according to the equation



Second, through contact with the ore undergoing reduction, it may deposit carbon



Because of the importance of this second reaction in the present study as well as in the blast-furnace process, tests were made to observe the effect of temperature and pressure on carbon deposition. Carbon monoxide was passed over previously reduced cubes at temperatures from 400° to 1000° C. and at pressures of one and two atmospheres. After the cube of ore had been completely reduced at 1000° C., both ends of the reduction furnace were closed and the temperature lowered to the desired level. After 20 min. had been allowed for the cube to attain uniform temperature, carbon monoxide was passed over it for 30 min. at the rate of 600 c.c. per minute.

A comparison of the extent of carbon deposition at the various temperatures and the two pressures is shown in Fig. 3. The units adopted in Fig. 3, carbon deposited per minute, are perfectly arbitrary and apply only to the conditions of this experiment.



The two curves of Fig. 3 show that doubling the pressures in the system practically doubles the rate of carbon deposition. A distinct maximum in the rate of carbon deposition can be noticed between 500° and 600° C., with the rate decreasing rapidly above and below this range, reaching almost negligible proportions at 400° and 1000° C. The deposited carbon was of a fine powdery type and of very low density. A cube surrounded by deposited carbon is shown in Fig. 4.

Previous work<sup>2,3</sup> has indicated that the optimum temperature for carbon deposition is considerably lower than that obtained in this

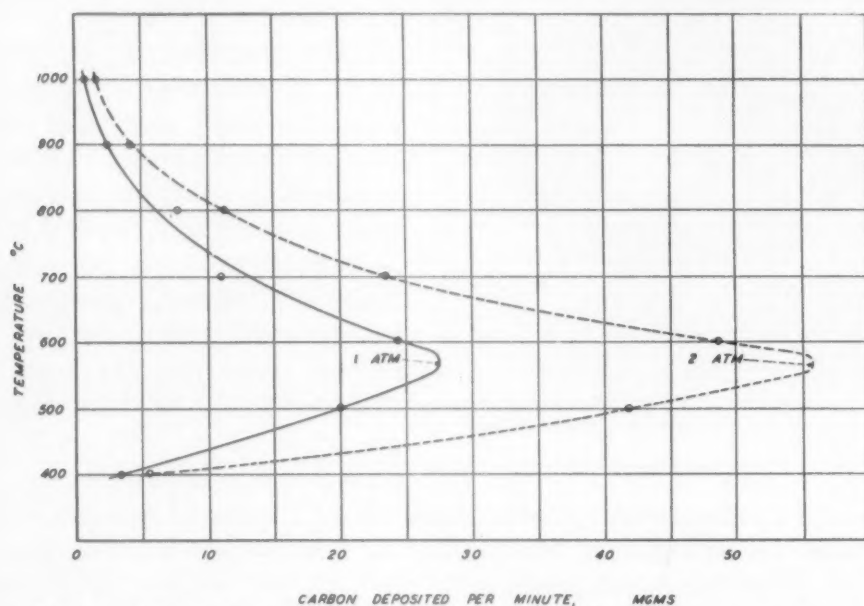


FIG. 3.—EFFECT OF TEMPERATURE AND PRESSURE ON CARBON DEPOSITION.

investigation. This discrepancy, however, can be attributed partly to the difference in the experimental conditions and partly to the difference in the type of ore. Moreover, in this work the deposition of carbon was measured in the presence of freshly reduced metallic iron, while the previous work was carried out in the presence of the magnetic oxide.

The effect of carbon deposition on the reducibility of iron ores in the blast furnace is a debatable subject. That a certain amount of carbon impregnates the lumps of ore is certain, and it is reasonable to expect that material so deposited would increase the rate of reduction, particularly of large lumps. However, when excessive amounts of carbon are deposited on exterior surfaces, passageways for the flow of gas are plugged and working pressures become abnormally high.

In a later section of this paper, evidence will be presented to indicate that the presence of carbon dioxide exerts a marked influence toward inhibiting the carbon-deposition reaction. Thus, in the lower zones of the furnace where the concentration of carbon dioxide is small, the effect

of the high temperatures, as shown in Fig. 3, serves to minimize the amount of deposition. On the other hand, toward the upper portion of the shaft, where the lower temperatures favor the reaction, the tendency toward increased carbon deposition must be balanced somewhat by the comparatively high concentration of carbon dioxide. It is fortunate that inherent principles of operation tend to prevent excessive carbon deposition in the blast furnace.

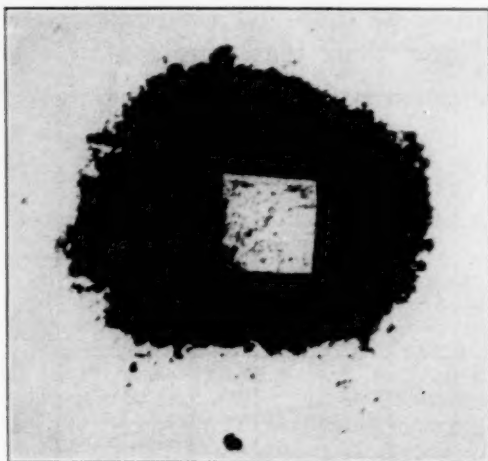


FIG. 4.—REDUCED CUBE SURROUNDED BY CARBON DEPOSITED IN THIRTY MINUTES AT 600° C.

#### REDUCTION OF CUBES OF IRON ORE

The preceding paper<sup>1</sup> on the effect of pressure on the rate of reduction dealt only with reduction by pure hydrogen. In order to simulate blast-furnace conditions more closely, several series of reductions were carried out, using the following gases or gas mixtures for the reaction: (1) carbon monoxide, (2) bosh gas (35CO, 65N<sub>2</sub>), (3) blast-furnace gas (CO, 28.4; CO<sub>2</sub>, 8.2; N<sub>2</sub>, 63.3).<sup>\*</sup> A comparison of the

rates of reduction with hydrogen and carbon monoxide was also made.

*Reduction with Carbon Monoxide.*—As a result of the work done on carbon deposition, a temperature of 1000° C. was selected as the most favorable to carry out the reductions in this investigation. The results of a portion of the tests with carbon monoxide have been plotted in Fig. 5. It is evident that the use of pressure materially increased the rate of reduction. The curves can be separated into two groups, according to the pressure employed during the reduction. Table 1 shows the average results of 22 reductions carried out with pure carbon monoxide. As in previous work, the time required for 90 per cent reduction has again been selected as an index of reducibility for the two conditions. The average time required for 90 per cent reduction at two atmospheres was 23 per cent less than that required at one atmosphere.

*Reduction with Pure Hydrogen at 1000° C.*—In order to compare the rates of reduction with hydrogen and with carbon monoxide, four cubes were reduced in hydrogen at 1000° C. and at pressures of one and of two atmospheres. These tests with hydrogen and the average results with carbon monoxide are compared in Fig. 6. The extreme difference between the rates of reduction with hydrogen and with carbon monoxide

<sup>\*</sup> Hereafter in this paper this gas mixture will be referred to as "blast-furnace gas."

is the most striking feature of this figure. The rate of reduction with hydrogen is about four times as fast as with carbon monoxide.

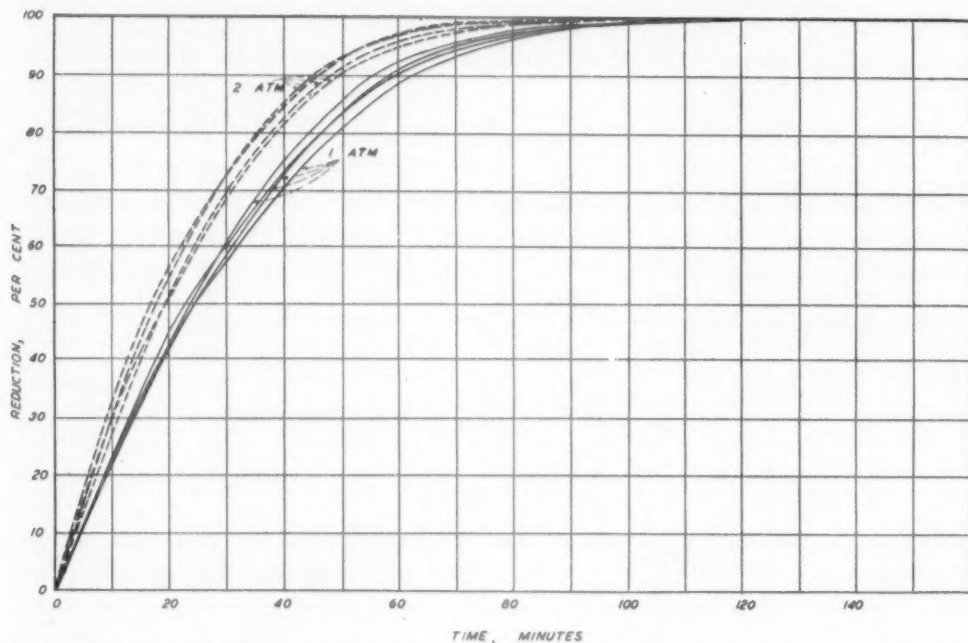


FIG. 5.—EFFECT OF PRESSURE ON TIME OF REDUCTION WITH CARBON MONOXIDE AT 1000° C.

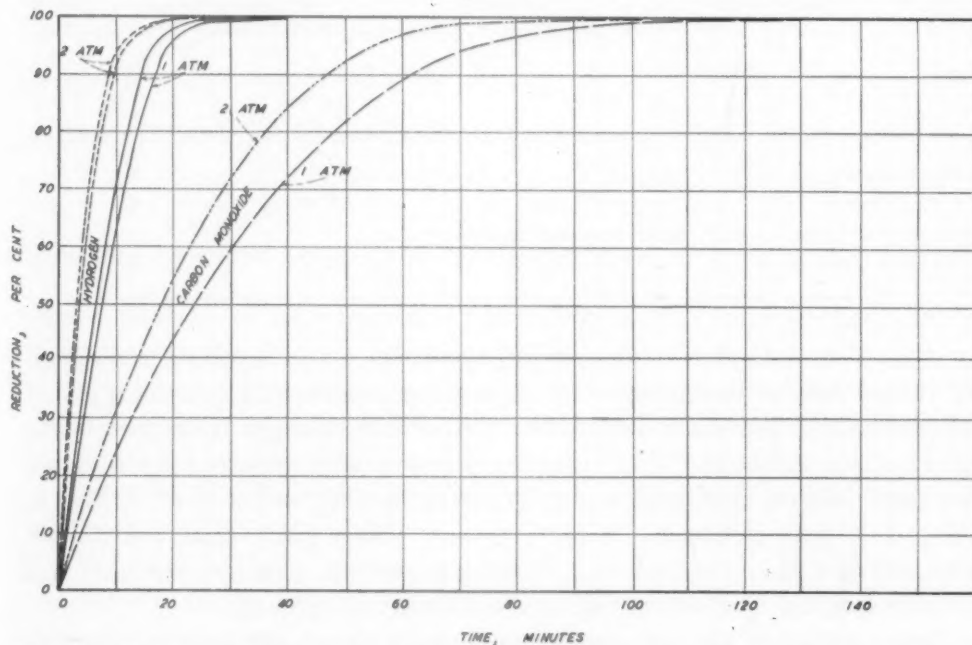


FIG. 6.—EFFECT OF PRESSURE ON TIME OF REDUCTION WITH HYDROGEN AND WITH CARBON MONOXIDE.

Another interesting feature of Fig. 6 is the fact that the increase in the rate of reduction with hydrogen due to the doubled pressure was

TABLE 1.—*Effect of Pressure on Time of Reduction with Carbon Monoxide*

Time, Min.	Average Percentage of Reduction		Time, Min.	Average Percentage of Reduction	
	1 Atm.	2 Atm.		1 Atm.	2 Atm.
0	0	0	70	94.1	99.0
10	26.0	31.8	80	96.9	99.7
20	44.1	54.5	90	98.5	99.9
30	69.8	71.4	100	99.5	100.
40	72.4	84.1	110	99.8	
50	81.7	92.2	120	99.9	
60	89.3	96.8	130	100.	
			Time for 90 per cent reduction, min....	61	47

40 per cent, which is practically the same as the value obtained in the previous work at 800° C. The average time required for 90 per cent reduction with the two gases is compared in Table 2.

TABLE 2.—*Reduction with Hydrogen and with Carbon Monoxide*

Pressure	Average Time Required for 90 Per Cent Reduction, Min.	
	H <sub>2</sub>	CO
1 atmosphere.....	15	61
2 atmospheres.....	9	47
Decrease in time of reduction due to doubled pressure, per cent.....	40	23

*Reduction with Bosh Gas.*—As an approach toward actual conditions within a blast furnace, a series of reductions was carried out using gas of approximately the same analysis as that which emerges from the tuyere zones of the furnace. The reducing mixture was prepared by diluting the pure carbon monoxide used in the preceding work with a known volume of pure nitrogen. The resultant "bosh gas" analyzed 35 per cent CO and 65 per cent N<sub>2</sub>. Reductions were made with bosh gas according to the procedure followed with carbon monoxide.

The results of the reductions with bosh gas have been plotted in Fig. 7. Again, the curves can be separated into two groups according to the pressure used during the reduction. The relation between the rates of reduction at one and at two atmospheres is about the same for bosh gas as for carbon monoxide. The absolute rate of reaction for

bosh gas, however, is approximately one-half that of carbon monoxide. The data plotted in Fig. 7 are summarized in Table 3.

Doubling the pressure decreased the time required for 90 per cent reduction by 20 per cent, which is somewhat less than the 23 per cent decrease with carbon monoxide.

*Reductions with Blast-furnace Gas.*—In all of the preceding work the reducing gas contained carbon monoxide greatly in excess of the equilibrium composition. However, the gas stream in some parts of the blast furnace may approach the equilibrium composition. A series of reductions was accordingly made to study the effect of pressure on

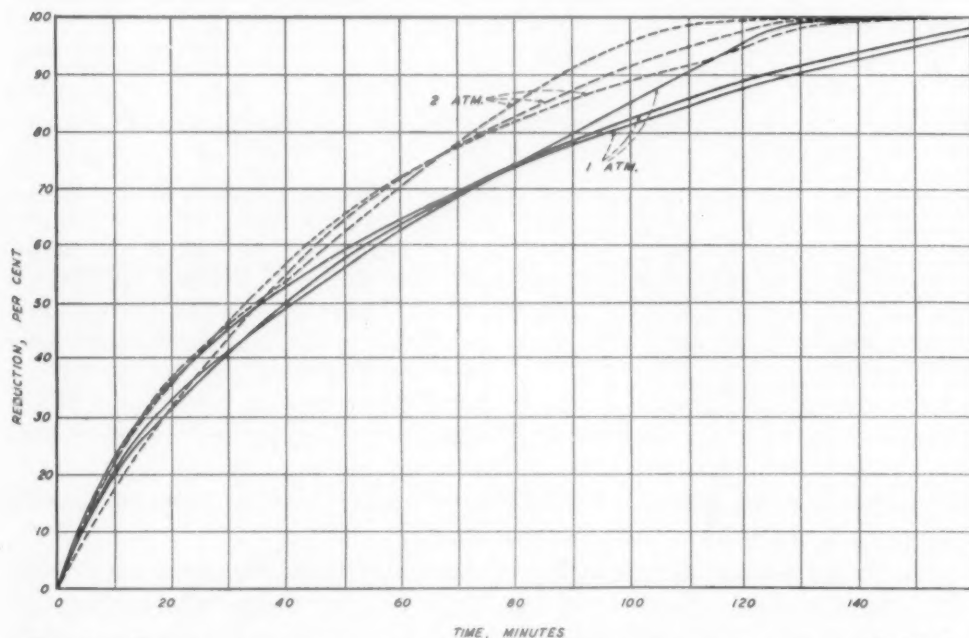


FIG. 7.—EFFECT OF PRESSURE ON TIME OF REDUCTION WITH BOSH GAS AT 1000° C.

the reduction of iron ore in a gas mixture approaching the equilibrium composition.

As Austin<sup>4</sup> pointed out, the equilibrium ratio CO to CO<sub>2</sub> for the FeO-Fe system is about 2.5 to 1 at 1000° C. In order to approach the equilibrium composition but still have a reducing atmosphere, a gas mixture of the following analysis was prepared: CO, 28.4 per cent; CO<sub>2</sub>, 8.2; O<sub>2</sub>, 0.1; N<sub>2</sub>, 63.3.

In order to carry out this part of the investigation, it was necessary to modify the reduction apparatus. The preheating furnace and the ascarite tower were removed from the circuit, leaving only the dehydrating tower in the line ahead of the reduction furnace. Since a certain amount of carbon dioxide was introduced with the reducing gas, it was no longer feasible to follow the course of reduction by the amount of carbon dioxide in the exit gases. However, by holding the carbon



dioxide in the entering gas constant it was possible to follow reduction by analyzing the gas leaving the reduction furnace.

With a flow of 600 c.c. per minute, the exit gas was analyzed for carbon dioxide every 5 min. for the first 20 min., every 10 min. for the next 40 min. and every 30 min. thereafter. When the carbon dioxide content of the exit gas corresponded with that of the original gas analysis plus a small allowance for carbon deposition, the reduction was considered complete. Although this method was neither as positive nor as accurate as that previously employed, nevertheless it gives some indication of the

TABLE 3.—*Effect of Pressure on Time of Reduction with Bosh Gas*

Time, Min.	Average Percentage of Reduction		Time, Min.	Average Percentage of Reduction	
	1 Atm.	2 Atm.		1 Atm.	2 Atm.
0	0.	0	120	90.8	96.8
20	33.3	34.9	140	95.2	99.2
40	50.1	54.7	160	97.7	99.9
60	63.5	70.7	180	99.6	100.
80	72.9	83.0	200	100.	
100	82.7	92.1			
			Time for 90 per cent reduction, min....	118	94

effect of increased pressure on the rate of reduction with a gas containing substantial amounts of carbon dioxide.

A closed circuit, shown in Fig. 8, was used in all the tests made with blast-furnace gas. Because of the large volume of the gas holder, the amount of carbon dioxide formed by reduction had a negligible effect upon the composition of the gas in the system.

After the completion of all the reductions in this series, the carbon dioxide content of the gas had not even increased 0.1 per cent.

In contrast to previous tests, doubling the pressure did not increase the rate of reduction. Although the first stages of reduction were definitely accelerated by the increased pressure, the rate slowed down so markedly in the latter stages that the time required for 90 per cent reduction was actually longer at the higher pressure (Fig. 9). Smaller cubes were used in this series of tests to reduce the over-all time required for each test.

It is evident, from the average data given in Table 4, that the time required for 90 per cent reduction was actually increased 24 per cent by doubling the pressure. The absolute rate of reduction of the ore cubes was decreased by approximately one-half with 8.2 per cent CO<sub>2</sub> compared with bosh gas.

No definite conclusions can be drawn from these few tests. The volume of three of the four cubes reduced at the higher pressure decreased

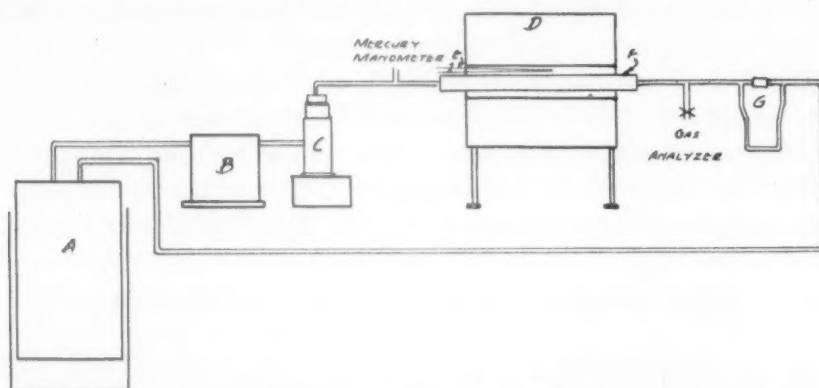


FIG. 8.—APPARATUS USED FOR REDUCTIONS WITH BLAST-FURNACE GAS.

- |                       |                    |
|-----------------------|--------------------|
| A. Gas holder.        | E. Thermocouple.   |
| B. Pump.              | F. Vitreosil tube. |
| C. Drying tower.      | G. Flowmeter.      |
| D. Reduction furnace. |                    |

markedly during reduction. The effect of this shrinkage on diffusion rates may have been sufficient to confuse the results. It would seem,

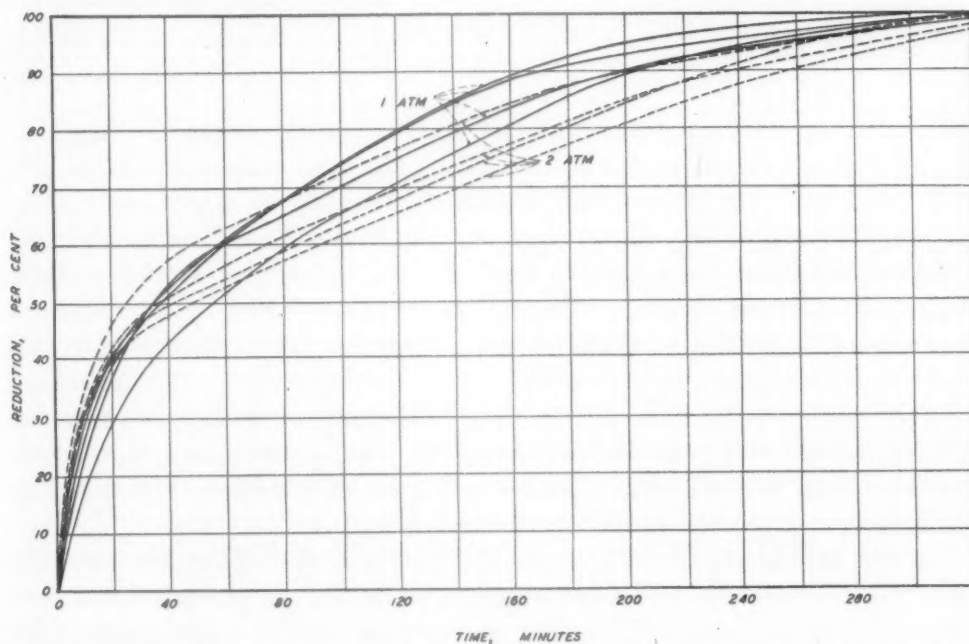


FIG. 9.—EFFECT OF PRESSURE ON TIME OF REDUCTION WITH BLAST-FURNACE GAS AT 1000° C.

however, from this work that as the reducing mixture approaches an equilibrium composition pressure is less effective in accelerating the reduction of iron ore. This tendency is in agreement with a later theoretical discussion.

*Appearance of Cubes after Reduction*

An interesting feature of this work was the appearance of the cubes after reduction in the various environments. Fig. 10 shows typical examples of the results of the various reductions. Cube *A* is an example of the original unreduced specimens and was included in the photograph merely for comparative purposes. Cube *B* was reduced by pure carbon monoxide at 1000° C. and immediately removed from the furnace. This cube shows a slight decrease in volume and a number of small cracks

TABLE 4.—*Effect of Pressure on Time of Reduction with Blast-furnace Gas*

Time, Min.	Average Percentage of Reduction		Time, Min.	Average Percentage of Reduction	
	1 Atm.	2 Atm.		1 Atm.	2 Atm.
0	0	0	140	80.8	73.9
20	36.1	42.0	160	85.0	77.7
40	49.4	51.2	180	88.7	81.4
60	58.2	56.6	200	91.7	84.8
80	65.0	61.4	220	99.5	87.7
100	70.8	65.8	240		90.7
120	75.9	70.0	300		97.7
			Time for 90 per cent reduction, min....	190	236

acquired during reduction. Cube *C* was also reduced completely at 1000° C. but was then held at 600° C. for 30 min. while pure carbon monoxide passed over it. During this latter period this cube was impregnated and coated with carbon to such an extent that its original features are no longer discernible. The over-all volume also increased considerably. It is impossible in the photograph to distinguish between the deposited carbon and the ore specimen. In this specimen, the carbon impregnation was so severe that one corner of the cube had actually broken away from the remainder of the piece.

Cube *D* was reduced by bosh gas at 1000° C. With the possible exception of a slightly greater degree of cracking, it is very similar to cube *B*. Cube *E* was reduced by hydrogen at 1000° C. Like the cubes reduced with carbon monoxide, it shows a small decrease in volume. However, the hydrogen-reduced cubes displayed little tendency to crack during reduction, and had a smooth surface after reduction.

Cube *F*, reduced with blast-furnace gas containing 8.2 per cent CO<sub>2</sub>, underwent the greatest change during reduction. The volume of the cubes decreased almost 50 per cent, and they acquired a semifused

appearance. Deep shrinkage cracks developed and in two instances the cubes spalled.

It is interesting to correlate the extent of shrinkage and the amount of carbon deposited. A reduction in volume occurred in all cases except those of abnormally high carbon deposition. This decrease in volume is attributed to a certain amount of sintering, which took place at the rather high temperature of reduction. Finely divided carbon deposited in the pores and on the surface of the cube minimized sintering and shrinkage. Meyer<sup>5</sup> also observed this in his work on the reduction of iron ores.

A certain amount of cracking was noticed in the cubes after reduction with carbon monoxide. Cracking probably occurred as a result of the

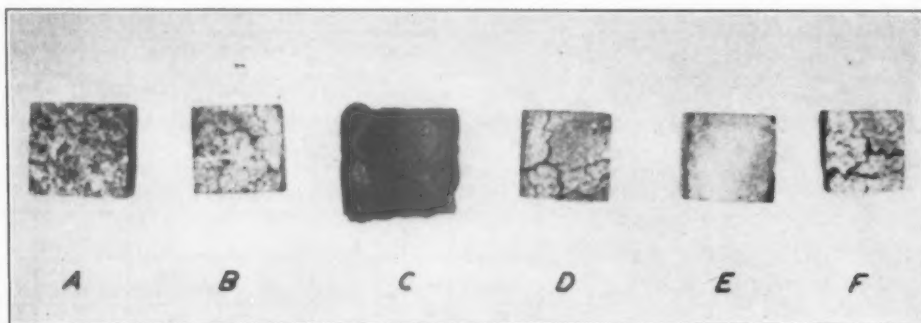


FIG. 10.—APPEARANCE OF CUBES AFTER REDUCTION.

carbon deposited within the piece (impregnated carbon). It seems reasonable to expect that the deposition of carbon in the limited volume available within the pores of the sponge iron would tend to produce such cracks. The formation of such cracks during the reduction would expose fresh surfaces to the reacting gas and should accordingly increase the over-all rate of reduction. From this point of view, a certain amount of carbon deposition might be desirable in smelting coarse ores.

It is significant that the cubes reduced with hydrogen showed no signs of cracking during reduction. There was, of course, no action similar to that of deposited carbon. It might be expected that a comparatively large decrease in volume would take place during reduction with hydrogen, as there would be no deposited carbon to retard sintering. However, the hydrogen-reduced cubes contracted in volume about the same as those reduced with carbon monoxide. The lengths of time that the cubes were at the high temperature must be considered. The hydrogen-treated cubes were held at 1000° C. from one-half to one-third as long as the cubes reduced with carbon monoxide. Had the hydrogen-reduced cubes remained at the temperature of reduction for a longer period of time, probably a greater amount of sintering would have occurred.

The extreme reduction in volume observed in cubes reduced in a gas containing substantial percentages of carbon dioxide may be attributed

to the lack of deposited carbon and its action in retarding sintering. With over 8 per cent  $\text{CO}_2$  in the reducing gas, it is natural to expect that the amount of carbon deposited would be much less than with bosh gas or pure carbon monoxide. The large amount of sintering is due to the long time required for reduction and to the absence of deposited carbon. This sintering was especially noticeable in the cubes reduced at the higher pressure. Severe cracking and spalling were probably the result of extreme changes in volume during reduction.

#### SUMMARY OF EXPERIMENTAL DATA

The data obtained in this investigation are summarized in Fig. 11 and Table 5. Each of the four pairs of curves in Fig. 11 represents an

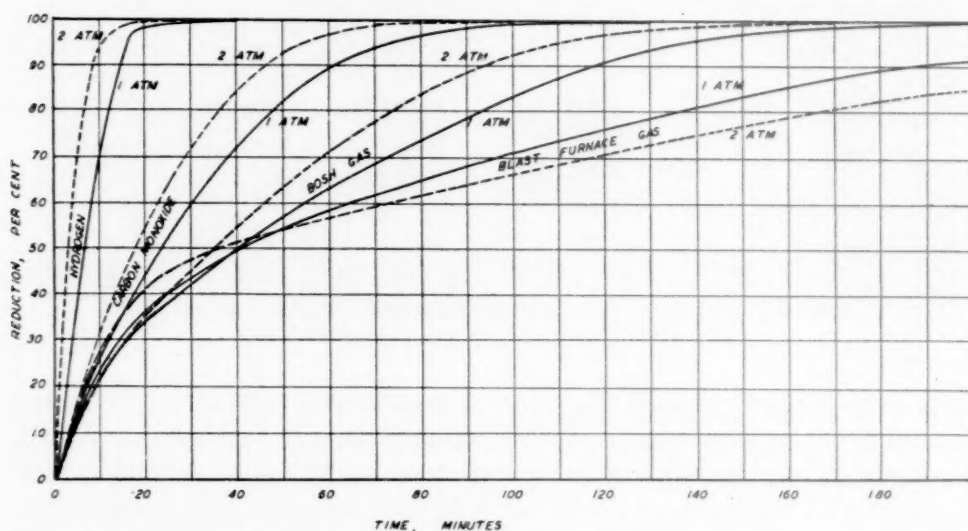


FIG. 11.—AVERAGE EFFECT OF PRESSURE ON TIME OF REDUCTION WITH VARIOUS GASES AT  $1000^{\circ}\text{C}$ .

TABLE 5.—Effect of Doubling Pressure on Time of Reduction at  $1000^{\circ}\text{C}$

Reducing Gas	Minutes Required for 90 Per Cent Reduction			
	1 Atm.	2 Atm.	Decrease	Percentage Decrease
Hydrogen.....	15	9	6	40
Carbon monoxide.....	61	47	14	23
Bosh gas <sup>a</sup> .....	118	94	24	20
Blast-furnace gas <sup>b</sup> .....	190	236		

<sup>a</sup> 65 per cent  $\text{N}_2$ , 35 per cent  $\text{CO}$ .

<sup>b</sup> 63.3 per cent  $\text{N}_2$ , 28.4 per cent  $\text{CO}$ , 8.2 per cent  $\text{CO}_2$ , 0.1 per cent  $\text{O}_2$ .

average of all the reductions made with the reducing gas indicated. Data concerning the time required for 90 per cent reduction are shown in Table 5. The experimental data may be summarized as follows:



1. The most rapid rate of reduction was obtained with hydrogen. The rate of hydrogen reduction was increased 40 per cent by doubling the pressure.

2. The rate of reduction with pure carbon monoxide was about one-fourth of that with pure hydrogen. Doubling the pressure of pure carbon monoxide increased the rate of reduction by about 23 per cent.

3. The dilution of carbon monoxide with sufficient nitrogen to form bosh gas lowered the rate of reduction by one-half. Doubling the pressure of bosh gas increased the rate of reduction about 20 per cent.

4. Finally, the substitution of 8.2 per cent of carbon dioxide for an equal portion of carbon monoxide in the bosh gas reduced the rate of reduction still further. Doubling the pressure during reductions with this gas increased the rate of reduction during the initial stages of the process but tended to decrease the over-all rate. These results indicate that the use of pressure would be most effective when applied to strongly reducing gases, rather than to those approaching equilibrium compositions.

#### APPLICATION OF KINETICS TO EXPERIMENTAL RESULTS

The reduction of iron ore and carbon deposition are based on heterogeneous reactions. In order to interpret the results of this investigation, an application is made of the kinetics of heterogeneous reactions. These heterogeneous reactions do not proceed merely through mechanical impact of gaseous molecules with the solid surface, but through the medium of a unimolecular film of the reacting gas. This adsorbed film should be considered as the source of the reaction; the surrounding gas phase is entirely removed from direct participation in the reaction. According to Hinshelwood,<sup>6</sup> the gas merely acts "as a reservoir which regulates the concentration in the adsorbed film."

It is a reasonable assumption that in the shaft of the iron blast furnace a condition similar to equilibrium between the gas phase and the adsorbed molecules is established rapidly compared to the actual rate of chemical changes undergone by the adsorbed molecules. If this assumption is accepted, it is possible to apply Langmuir's<sup>7</sup> mathematical analysis to blast-furnace reactions.

By equating the rates of condensation onto the surface to the rate of evaporation from it, Langmuir derived the following expression for the fraction of a solid surface,  $\sigma$ , covered with adsorbed gas:

$$k_1 p(1 - \sigma) = k_2 \sigma \quad [3]$$

or

$$\sigma = \frac{k_1 p}{k_2 + k_1 p} = \frac{p}{\frac{k_2}{k_1} + p} \quad [4]$$

where  $p$  represents the pressure of the gas phase and  $k_2/k_1$  is a constant which must be determined from experimental data.

Hinshelwood<sup>6</sup> has pointed out that for each reaction there probably exists a definite saturation limit, which determines the degree to which adsorption can take place. Therefore, the preceding equation can be considered in the light of the two limiting conditions, namely: (1) when the adsorption is very slight, (2) when the entire surface is nearly saturated.

When the adsorption is slight, the term  $1 - \sigma$  is approximately equal to unity and thus

$$\sigma = \frac{k_1}{k_2} p \quad [5]$$

Therefore, for the first limiting case, the fraction of the solid surface covered with adsorbed gas is directly proportional to the pressure. Consequently, the reaction rate for such conditions, which is proportional to the fraction of the surface covered, would also be proportional to the pressure.

When the entire surface is nearly saturated,  $\sigma$  is approximately equal to unity, and the reaction rate becomes equal to a constant, independent of the pressure.

Hinshelwood has also pointed out that the law of mass action holds for heterogeneous reactions, but the pressure of the gas cannot be considered as the active mass. Instead, only the gas adsorbed is in a position to react, and it is this concentration that must be considered with the mass action principle.

#### KINETICS OF THE CARBON-DEPOSITION REACTION

In general, gas-solid reactions do not coincide with either of the two previously mentioned special cases, but occur in some intermediate manner. The carbon-deposition reaction is essentially a bimolecular process; that is, two molecules must combine in order to react. Since the chance that two molecules occupy adjacent positions on the surface depends on the square of the surface concentration, the rate of reaction would be proportional to the square of the expression given for  $\sigma$ . For the general case,  $\sigma$  was equal to  $\frac{k_1 p}{k_2 + k_1 p}$ . Therefore, we can express the rate of carbon deposition,  $dC/dt$ , by the equation

$$\frac{dC}{dt} = k \left( \frac{k_1 p}{k_2 + k_1 p} \right)^2 = \frac{k p^2}{(1 + b p)^2} \quad [6]$$

where both  $k$  and  $b$  are arbitrary constants. According to this equation, the rate increases less rapidly than the square of the pressure. An approximate equation can therefore be substituted

$$\frac{dC}{dt} = kp^n \quad [7]$$

where  $n$  is some value greater than unity. Such an expression is in agreement with the results obtained in this investigation. Since by doubling the pressure, a twofold increase in the rate of carbon deposition was obtained, it is evident that under the conditions of this experiment the value for  $n$  closely approaches 2.

In order to approach more closely the conditions that actually existed during carbon deposition, the adsorption of the carbon dioxide produced by the reaction must be considered. Such a consideration results in a more complicated equation but one similar to those that have been considered. In addition, the constant flow of gas maintained in the present experiments reduced the partial pressure of the carbon dioxide in the gas phase to negligible proportions. The amount of carbon dioxide adsorbed was accordingly so small that its adsorption can be neglected, as in equation 7.

#### KINETICS OF THE REDUCTION REACTION

Since the reduction of iron ores by carbon monoxide is unimolecular, the rate of formation of  $\text{CO}_2$ ,  $d\text{CO}_2/dt$ , would be proportional to the fraction of the surface occupied by the reducing gas. In equation 4, this fraction was given by the expression  $\frac{k_1p}{k_2 + k_1p}$ . Therefore, the rate of reduction can be expressed as

$$\frac{d\text{CO}_2}{dt} = k \frac{k_1p}{k_2 + k_1p} \quad [8]$$

or

$$\frac{d\text{CO}_2}{dt} = \frac{kp}{1 + bp} \quad [9]$$

An exponential approximation of this equation yields the following result:

$$\frac{d\text{CO}_2}{dt} = kp^n \quad [10]$$

where  $n$  is a number less than unity, varying with the degree of adsorption. Equation 10 can be used to explain the differences between the effect of pressure on the reduction with hydrogen as compared with carbon monoxide. The small departure of the rate of reduction with hydrogen from a linear relation with pressure would indicate that the adsorption of that gas was comparatively weak. On the other hand, simple calculations from the results of the work on carbon deposition

demonstrate that the carbon monoxide is moderately adsorbed on the freshly reduced iron surface; and it is reasonable to expect that such a condition would also exist on the reacting interface between the iron and the unreduced oxide. These differences in the adsorption tendencies would be reflected in distinctly varying values of  $n$  in equation 10 and, consequently, serve to explain the results obtained with the strongly reducing gases. Again, in these considerations, no mention was made of the adsorption of the product of the reaction. Since the adsorption of these products was minimized by their constant removal from the reduction tube, no serious errors were introduced by omitting this factor from the preceding consideration.

However, in the reductions with blast-furnace gas, there was always an appreciable percentage of the products of the reaction present, and its adsorption can no longer be omitted from these considerations. In order to aid in the explanation of the retarded effect of pressure on the rate of reduction with the preceding gas mixture, an application is made of Hinshelwood's<sup>6</sup> analysis to the case under consideration. As in previous analyses, equilibrium between the gas phase and the adsorbed film is assumed.

For the gaseous product the equation would take the form of

$$k_1 P_{\text{CO}_2} (1 - \sigma - \sigma') = k_2 \sigma' \quad [11]$$

where  $P_{\text{CO}_2}$  represents the partial pressure of the product and  $\sigma'$  the fraction of the surface occupied by it. For the general case where both the reacting gas and the product are moderately adsorbed, the equations are slightly more involved than those previously cited. The intermediate analysis is analogous to the preceding derivations and has been omitted. The resulting equations have been simplified by approximations, and the reaction rate can be expressed in the form

$$\frac{d\text{CO}_2}{dt} = \frac{k P_{\text{CO}}^n}{P_{\text{CO}_2}} \quad [12]$$

where  $n$  depends on the degree of adsorption of both the reactant and the resultant gases and is no longer restricted to values less than unity.

Equation 12 can be used to explain effect of pressure in retarding the reaction rate when the reduction was carried out by the blast-furnace gas mixture. The presence of an appreciable concentration of carbon dioxide in that mixture brought about conditions that more nearly approached those assumed in the derivation of equation 12. In this equation, as the value of  $n$  approaches unity, the rate of reduction decreases accordingly. Furthermore, when the exponent becomes less than unity, an increase in pressure would actually result in a decrease in the reaction rate. The results of the tests with blast-furnace gas indicate that the value of  $n$  is less than unity. However, as previously



mentioned, intense sintering took place during these reductions. The slower over-all rate of reduction at two atmospheres with blast-furnace gas may have been due partly to greater compactness of the cubes and partly to greater adsorption of carbon dioxide.

If an application of the derivation leading to equation 12 is made to the reductions with bosh gas, it can be seen that the adsorption of nitrogen on the reacting surface is weak. In these considerations, the adsorption of nitrogen would enter the equations in the form of a term similar to  $\sigma'$  of equation 11. By an analysis such as that followed previously, it could be demonstrated that the resultant effect of any appreciable adsorption of nitrogen would be to reduce the effect of pressure on the reaction rate. Since the effect of pressure on the rate of reduction was practically the same with bosh gas as with carbon monoxide, the amount of nitrogen adsorbed must have been small.

The authors fully realize that the equations and the conditions briefly considered in this theoretical discussion are, at best, rough approximations. In actual operation, far too many variables are involved to be included in any such simple analysis. An attempt has been made, however, to interpret experimental data, to point out important features of the reduction process, and to indicate the manner in which pressure may influence gas-solid reactions.

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#### DISCUSSION

(H. W. Johnson presiding)

D. E. BABCOCK,\* Pittsburgh, Pa.—The authors of this paper have done a fine piece of work. Its values and benefits will be reaped for a long time to come, and in proportion to the effort put forward in its direct applications to blast furnace or other operations involving reaction chemistry concerned.

It is worthy of special note that the relative velocities of reduction of iron oxide by hydrogen and carbon monoxid are of the order of 4 to 1. Graham's law for the rates

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\* Industrial Fellow, Mellon Institute of Industrial Research.



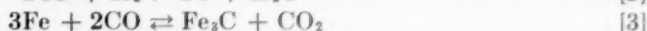
of diffusion of gases shows them to be proportional to the reciprocal of the square roots of their molecular weights. This gives the following results:

$$\frac{1}{\sqrt{H_2}} = \frac{1}{\sqrt{2}} = 0.707 \quad 3.73/1.00$$

$$\frac{1}{\sqrt{CO}} = \frac{1}{\sqrt{28}} = 0.189$$

Hence, if diffusion were the slowest reaction involved in these reductions, the relative reaction rate should have the exact relationship found by the authors, as is true.

Of interest further in this discussion, since the effect of pressure operations is of major importance to the blast-furnace operator, is the observation that the completeness of the reaction was not affected appreciably by pressure, but carbon deposition was markedly affected. It might well be noted that in any chemical reaction or reaction equilibrium, the application of pressure to it causes a shift in the equilibrium in a direction that will relieve the pressure so applied. This is Le Chatelier's principle and means that if the products of a reaction have a smaller total volume than the reactants the pressure will favor the movement of the reaction toward its completion. In the these reactions:



it may be noted that reactions 1 and 2 are not affected by pressure, since the volumes of the reactants are identical with the volumes of the products formed. However, in equation 3 the products of the reaction are less by one molar volume than the reactants, and increased pressure will have a marked effect on this reaction in moving it toward the right by increasing the amount of carbon deposited as iron carbide and increasing amount of carbon dioxide formed. When these facts are applied to practical blast-furnace operations, the conclusions may be drawn that increased pressures will (1) not materially affect the direct reduction of iron oxide by either hydrogen or carbon monoxide; (2) increase markedly the amount of carbon deposition in the furnace. The combined effects of these changes may slightly reduce reduction efficiencies and reduce the CO:CO<sub>2</sub> ratio to some small extent.

G. E. STEUDEL,\* Chicago, Ill.—It is work of this nature that leads to new ideas and improves operating practice. I think more determinations between the temperatures of 400° to 1000°C. with gas as actually exists in the furnace would give a more exact picture of the effect of pressure regarding ore reduction in the blast furnace. From these results more specific calculations could be made in comparing the metallurgical advantages with the mechanical difficulties with increased pressure.

M. TENENBAUM AND T. L. JOSEPH (authors' reply).—The authors believe that the reduction process is too complicated to attribute differences in reaction rates solely to differences in the rates of diffusion of the reacting gases. It is known, for example, that the specific rates of reaction are not the same for all gases even though the concentrations at the reacting surface are comparable. The diffusion of the products of the reaction introduces another complication. Until more positive evidence is available, the cause for the observed differences in the rates of reduction with hydrogen as compared to carbon monoxide cannot be determined definitely.

The law of mass action is perfectly valid for heterogeneous reactions. These reactions do not, however, proceed merely through mechanical impact of gaseous

\* South Works, Carnegie-Illinois Steel Corporation.

molecules with the solid surface. An adsorbed unimolecular film is the immediate source of the reacting gas. The concentration of the gas in the adsorbed film must accordingly be considered. While it is true that the surrounding gas acts as a reservoir which regulates the concentration in the adsorbed film, there probably exists for every gas and for each solid surface a definite saturation limit that determines the degree to which adsorption can take place. The effect of pressure on reaction 3 might accordingly vary, depending upon the degree to which this saturation limit is approached. The Le Chatelier principle can be applied to heterogeneous reactions if the concentration of gas in the adsorbed film is considered.

Mr. Steudel's suggestion that additional work should be carried out at temperatures below 1000°C. is fully justified. Owing to excessive amount of carbon deposition that accompanies the reaction at the lower temperatures, it was not feasible to carry out reduction studies by the method described in the paper. However, a method has recently been developed whereby the effect of pressure on the rates of reduction at lower temperatures can be studied.

# Experimental Methods in the Study of Steelmaking

## ROUND TABLE

(New York Meeting, February 1939)

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### INTRODUCTION

ON Thursday morning, Feb. 16, 1939, a round table discussion was held on the subject of Experimental Methods in the Study of Steelmaking. Dr. John Chipman, Professor of Metallurgy at the Massachusetts Institute of Technology, and chairman of the A.I.M.E. Committee on Physical Chemistry of Steelmaking, presided. In opening the meeting, the chairman said:

"The purpose of this round table is to discuss methods of study by which more and better information on the fundamentals of steelmaking can be obtained. It was thought that a round table discussion rather than a symposium would furnish the best opportunity for those actually using various methods of study to get together and discuss their common problems. For this reason attention will be focused upon methods of study rather than upon their results. We want new and current and up-to-date discussion.

## LABORATORY METHODS

## SPECIAL ANALYTICAL METHODS

Dr. J. G. Thompson\* presented a paper on the Cooperative Study of Methods for Determination of Oxygen in Steel. The material of this paper is now available in the A.I.M.E. TRANSACTIONS (1937) 125, 246.

Improvements in the Accuracy of the Vacuum-fusion Method for the Determination of Oxygen in Steel

BY SHADBURN MARSHALL† AND JOHN CHIPMAN‡

The results of the recent study of methods for the determination of oxygen,<sup>1</sup> conducted by the National Bureau of Standards, in which 30 laboratories cooperated, showed the reliability of the vacuum-fusion method but indicated that more development work was necessary to eliminate a source of error inherent in the method when applied to certain types of steels.

Operators of vacuum-fusion analyzers are familiar with the so-called manganese or aluminum "interference" caused by distillation of these volatile elements and formation of metallic films that deposit in the cooler parts of the furnace when samples containing relatively large amounts of manganese or aluminum are analyzed. Von Seth<sup>2</sup> and Diergarten<sup>3</sup> reported manganese interference. Bardenheuer and Schneider<sup>4</sup> found no interference below 1 per cent Mn but Vacher and Jordan<sup>5</sup> reported interference when the manganese content of the metal exceeded 0.2 per cent. Hessenbruch and Oberhoffer<sup>6</sup> stated that the effect of metallic films could be diminished by faster removal of the gases from the furnace. Thanheiser<sup>7</sup> investigated the absorption of carbon monoxide by manganese under conditions simulating those existing in a vacuum-fusion furnace and reported that between the temperatures of 400° and 750°, carbon monoxide was rapidly absorbed by a distilled manganese film with the precipitation of carbon. Below 300° no precipitation of carbon was observed although absorption still occurred. Drastic cooling of the furnace walls did not eliminate the absorption.

Factors affecting manganese interference were discussed by the committee reviewing the results of the cooperative study reported by Thompson, Vacher and Bright.<sup>1</sup> It was found that higher oxygen recoveries, indicating lower losses, are obtained when the sample is rapidly melted, the gases evolved are rapidly removed from the

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‡ Professor of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

<sup>1</sup> Thompson, Vacher and Bright: Cooperative Study of Methods for the Determination of Oxygen in Steel. *Trans. A.I.M.E.* (1937) 125, 246.

<sup>2</sup> Von Seth: *Jernkontorets Ann.* (1928) 112, 113.

<sup>3</sup> Diergarten: *Archiv Eisenhüttenwesen* (1930) 3, 577.

<sup>4</sup> Bardenheuer and Schneider: *Mitt. K. W. I. Eisenforschung*, Dusseldorf (1931) 13, 215.

<sup>5</sup> Vacher and Jordan: *Nat. Bur. Stds. Jnl. of Research* (1931) 7, 375.

<sup>6</sup> Hessenbruch and Oberhoffer: *Rev. de Met.* (1929) 26, 93.

<sup>7</sup> Thanheiser: *Stahl und Eisen* (1936) 56, 1125; *Jnl. Iron and Steel Inst.* (1936) 84, 359.

highly evacuated furnace and when the manganese content of the metal in the crucible is kept low by dilution with manganese-free iron or when a fresh crucible is used for each sample.

In the "fractional" method introduced by Reeve<sup>8</sup> these conditions are not fulfilled, yet the results obtained by Hoyt and Schiel,<sup>9</sup> who employed this method in the cooperative study, agreed with other determinations with respect to total oxygen. They pointed out that the use of tin in the fractional method (to lower the melting point of the steel) resulted in the diminution or elimination of the manganese interference, presumably by covering or deactivating the distilled manganese.

The purpose of the present investigation was to study the effects of pumping speed and tin additions on the recovery of oxygen from the eight samples used in the cooperative study. Two analyzers of similar design were employed and each of these was rebuilt during the course of the investigation to provide greater speed of evacuation of the furnace. The first of these was built in the Research Laboratories of the American Rolling Mill Co. in 1935. It employed a two-stage mercury diffusion pump of about 2 liters per second capacity and the connection between furnace and pump was 16-mm. diameter at its narrowest point. Later two pumps were installed, the high-vacuum stage being an all-glass "umbrella type" pump of about 15 liters per second capacity.

The apparatus set up at the Massachusetts Institute of Technology during 1938 originally used a two-stage pump of about 2 liters per second capacity, which was replaced by two pumps. The high-vacuum stage is of the expanding jet type described by Copley and associates<sup>10</sup> and reported to have a capacity of 60 liters per second. The connection between furnace and pump was not less than 30-mm. diameter at any point.

The design of this equipment included a few special features that deserve mention. The samples were dropped magnetically from a simple glass holder and the evolved gas was pumped into a storage reservoir. When an extraction had been completed the gas sample was transferred to the analytical apparatus and the reservoir was then used to receive the gas from a second sample (or the next fraction of gas when using the fractional method).

The gas analysis was conducted as described by Chipman and Fontana<sup>11</sup> except that pressures were read on a butyl-phthalate manometer instead of the McLeod gauge. The vacuum side of the manometer was connected to the diffusion pump and was evacuated before the start of each run. This manometer has proved simpler and more rapid than the McLeod gauge and its accuracy is ample for the purpose.

A few changes in the furnace construction have led to appreciably lower blanks and ease of assembling. The furnace proper consists of the usual fused silica tube with a water-cooled brass collar to which the sample-holding head is cemented. Graphite powder is used to insulate the crucible and protect the silica tube in a modification of the method suggested by Sloman.<sup>12</sup> The crucible is embedded in graphite powder, 60 to 100 mesh, which is contained in an alundum thimble, 50-mm. inside diameter. The thickness of graphite powder around and underneath the crucible is about  $\frac{1}{4}$  in. The crucible is packed in the graphite powder in the thimble, which is then placed in the furnace on a bed of granular magnesite. The crucible is prepared by evacuation for at least an hour at a temperature well above 2000°C.

<sup>8</sup> Reeve: *Trans. A.I.M.E.* (1934) **113**, 82.

<sup>9</sup> Hoyt and Schiel: *Trans. A.I.M.E.* (1937) **125**, 313.

<sup>10</sup> Copley, Simpson, Tenney, Phipps: *Rev. Sci. Inst.* (1935) **6**, 265.

<sup>11</sup> Chipman and Fontana: *Ind. and Eng. Chem., Anal. Ed.* (1933) **7**, 391.

<sup>12</sup> Sloman: Sixth Report on the Heterogeneity of Steel Ingots, Iron and Steel Inst. (1935) 71.



The method of carrying out an analysis using tin may be described as follows: After the crucible has been sufficiently baked out the temperature is lowered to 1600°C. and a "blank" is collected and analyzed. The temperature is then lowered to 1300°C. and 10 to 20 grams of tin, together with an equal amount of low-manganese iron, are dropped into the crucible. The temperature is then raised to 1600° and the evolved gas is pumped away and discarded. During this time the walls of the furnace are being coated with a film of tin which is being vaporized from the melt. When the furnace pressure has returned to its initial value, indicating that the gas from the iron-tin alloy has been removed (about 10 min.), the first sample may be dropped into the crucible and outgassed in the usual manner. When the outgassing is complete and the collected gas has been transferred to the analytical train, another sample may be outgassed and stored in the reservoir. This procedure practically doubles the number of samples that may be analyzed in one day. The original tin addition is usually sufficient to maintain a vapor of tin in the furnace for the duration of any one day's run.

Table 1 contains the results obtained on the eight samples supplied for the cooperative study as obtained with each of the pump arrangements mentioned, both with and without tin. When no tin was used, the manganese content of the melt was kept below 0.50 per cent by dilution. When tin was used, no effort was made to keep the manganese content of the melt at a low value, except that the samples were usually analyzed in the order of increasing manganese content, whereby the manganese content of any one sample was, in effect, lowered by dilution by those that were outgassed previously. The low-manganese iron dropped with the tin also caused a slight diluting effect.

TABLE 1.—*Results Obtained on Eight Cooperative Samples with and without Tin at Three Different Pumping Speeds*

Sample No.	Oxygen, Per Cent							
	Per Cent Mn	Committee's Range	2 Liters per Sec.		15 Liters per Sec.		60 Liters per Sec.	
			No Tin	Tin	No Tin	Tin	No Tin	Tin
1	0.31	0.016-0.020	0.015	0.019	0.016	0.019	0.015	0.019
2	1.15	0.012-0.018	0.011	0.018	0.013	0.018	0.015	0.019
3	0.72	0.014-0.020	0.015	0.017	0.016	0.017	0.014 <sup>a</sup>	0.018
4	0.65	0.001-0.004	0.001	0.003	0.001	0.003	0.002	0.003
5	0.45	0.007-0.011	0.009		0.010	0.011	0.008	0.010
6	0.47	0.005-0.008	0.006		0.007	0.008	0.008	0.008
7	0.024	0.100-0.110	0.103		0.103	0.108 <sup>a</sup>	0.110 <sup>a</sup>	0.111 <sup>a</sup>
8	0.45	0.015-0.019	0.014	0.017	0.017	0.019	0.015	0.020

<sup>a</sup> Different lot of sample.

#### Results

The results are presented graphically in Fig. 1. The open circles represent results obtained without tin, the solid circles with tin; the pumping speed increases from left to right for each sample and the rectangles represent the committee's range of "acceptable" results.

Fig. 1 shows that the rate of removal of the gases from the furnace is an important factor when samples containing relatively large amounts of manganese are analyzed. Consideration of the samples in which no tin was used indicates that higher results are

obtained with higher pumping speeds. This effect is not so evident in samples 1, 5, 7 and 8, but these samples contain the smallest amounts of manganese. The effect of pumping speed is marked in sample 2, which contains 1.15 per cent Mn, and in number 4, which contains metallic aluminum.

The effect of tin is also readily apparent. In every case a higher result is obtained when tin is used, regardless of the pumping speed, and the effect is more pronounced the lower the pumping speed and the higher the manganese content. All the values obtained with the use of tin are near the top of the committee's range. Moreover, when tin is used the effect of pumping speed is much less noticeable. All of the results with tin at the two higher pumping speeds may be considered checks. Even at the lowest pumping speed, when tin is used four of the five results, including the

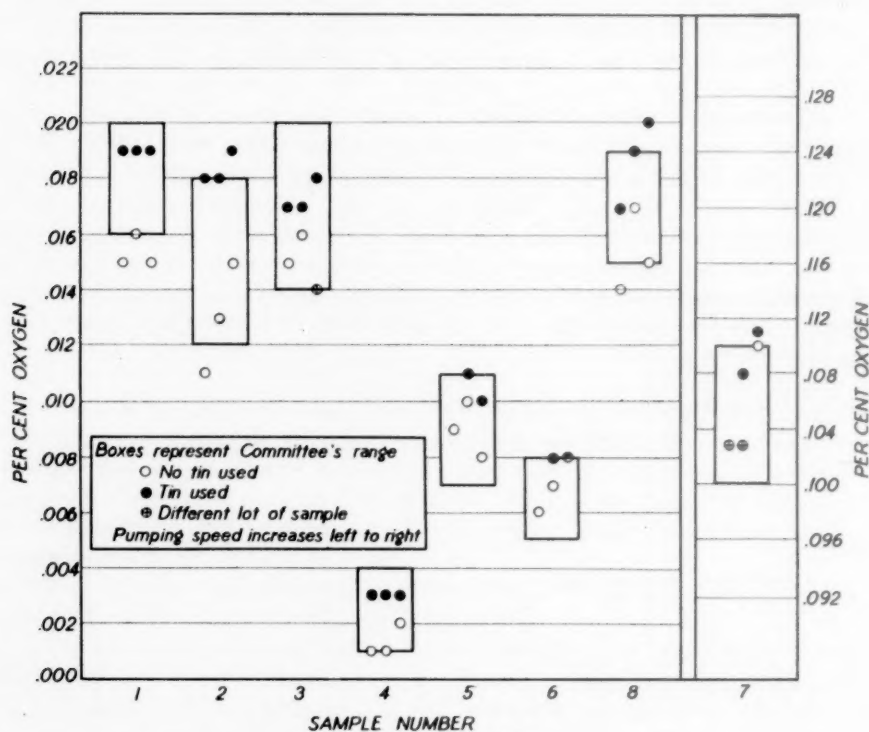


FIG. 1.—RESULTS.

three steels with highest manganese content, agree with those obtained with the high-speed pumps.

It is believed that the inconsistent results obtained on sample 8 may be due to a source of error mentioned by Chipman and Fontana,<sup>11</sup> which the presence of tin in the melt could not be expected to overcome. They state that with samples containing large percentages of  $Al_2O_3$ , there is a tendency for the sample to melt away from the alumina and leave part of it as a dry powder adhering to the crucible wall. It was noted that the error was increased by the presence of the graphite plug used to prevent spattering and minimized by lowering the sample into a molten residue from a previous analysis.

The results obtained with tin, even at the lowest pumping speed, are in excellent agreement with those recently reported for the same samples by Thompson and Holm<sup>13</sup> who used a four-stage diffusion pump and eliminated every possible restriction to rapid

<sup>13</sup> Thompson and Holm: Nat. Bur. Stds. *Jnl. of Research* (1938) **21**, 79.

removal of the gases from the furnace. This indicates that the error introduced by metallic films may be as effectively minimized by the addition of tin to the crucible as by introducing elaborate pumping arrangements.

#### *Summary*

An investigation has been made of the effect of pumping speed and the addition of tin to the crucible on the accuracy of oxygen analyses obtained by the vacuum-fusion method, especially with regard to samples of high manganese content. The results indicate that the error introduced by metallic films of vaporized metals may be minimized by the addition of tin in the manner described and by increased pumping speed, the former being the simpler.

#### *Discussion*

D. W. MURPHY,\* Ann Arbor, Mich.—We have introduced a rather minor variation in the fractional technique as developed by Hoyt, Scheil and Reeves, at the A. O. Smith Corporation. We found that tin prevented an accurate determination of temperature during the fractionation (we could not keep the sight window free from condensed tin vapor), therefore we have used Armeo iron as the initial charge, melting that at a temperature of approximately 2140°F., or about 1100°C. Under those conditions fairly good temperature readings can be obtained at any of three commonly determined fraction temperatures.

Our experience with this method has indicated that the various fractional values will usually repeat in check determinations within about the same range that can be expected for the total determination.

J. G. THOMPSON,† Washington, D. C.—A limited number of experiments made at the National Bureau of Standards, using tin, confirm the report that the presence of tin helps to eliminate interference by manganese vapor. I believe, however, that the results will vary with the individual apparatus; for example, with our apparatus the beneficial effect of the presence of tin is more pronounced at low pumping speeds than it is at higher pumping speeds. With our maximum pumping speed, the benefit of tin is that it permits the determination of three or four consecutive samples before the interference becomes pronounced, rather than a higher recovery of oxygen from the first sample that is run.

J. L. GREGG,‡ Bethlehem, Pa.—We have used a Thanheiser furnace, mentioned by Dr. Thompson (the carbon resistor furnace developed at the Kaiser Wilhelm Institute), for oxygen determinations for about two years, and it is giving very satisfactory results. We get very low blanks and the same oxygen values with the fractional analyses as with the total analyses, with or without tin. We use the four-stage Gaede pump, therefore evacuate rapidly.

#### **Quantitative Spectrochemical Analysis of Mixtures of Gases**

Prof. O. S. Duffendack§ spoke on the use of the spectrograph in the analysis of gases obtained in metallurgical processes. Much of the information he gave had already been published as a paper of which the following is an abstract.

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† National Bureau of Standards.

‡ Bethlehem Steel Co.

§ Professor of Physics, University of Michigan, Ann Arbor, Mich.

*Abstract\**

Difficulties commonly encountered in the spectroscopic analysis of mixed gases are that: (1) the relative intensities of spectral lines of the constituent gases may vary with the total pressure of the gas, even though the relative amounts of the constituents remain constant; (2) the proportions of the several constituents of a gas mixture will not remain constant when an electric discharge is maintained in the tube because of clean-up of gases by one or more of several agents; (3) variations in intensities of lines of certain elements can result from interference of atoms of another gas.

The solution of a number of these difficulties has resulted from: (1) the use of helium in excess as the carrier of the electric discharge and (2) the use of a small addition of argon as an internal control. The intensities of the argon lines remained remarkably constant even when considerable amounts of other gases were added to the mixture. Pressures of helium of from 2 to 8 mm. have been used successfully. In most of the work a pressure of 0.01 mm. for the added argon was found satisfactory. Gases whose amounts have been determined by this method are hydrogen, oxygen, nitrogen and carbon monoxide. Carbon dioxide, if present, must be separated and determined by some other method, since in the glow discharge it produces the bands of carbon monoxide.

*Discussion*

D. W. MURPHY.—We have met some of the troubles that Professor Duffendack discussed. We tried to adapt our vacuum-fusion outfit to the fractional determination of oxygen and for various reasons were obliged to decrease the size of the crucible used in the furnace. When that was done, a very serious glow discharge was obtained in the furnace during the run. This discharge apparently is a function of the pressure and the electrical coupling between the crucible and the coil. The glow is most pronounced at what might be called an intermediate pressure, and disappears at pressures below and above certain values.

This effect was so serious at one time that up to approximately 75 per cent of the gas evolved from a given steel could be lost by ionization, which occurs during the glow discharge and subsequent absorption of the ionized gas on the refractory walls, and so forth, in the furnace. That amounts to quite a sizable error. It appears to be eliminated by the use of crucibles with slightly heavier walls, or slightly longer crucibles, or in general by altering in some way the electrical coupling of the furnace. Operation at lower pressures during the major portion of the run is also beneficial.

Refractory shields in general are more likely to give this kind of trouble than the graphite shields we used for the most part in our work.

J. G. THOMPSON.—In regard to spectroscopic determination of gases, does the decrease in intensity of the lines of helium mean a clean-up of helium by reactions of some kind, or a solution of helium in the metal sample, or is it a question of ionization?

O. S. DUFFENDACK.—The reduction of the intensity of helium is certainly not due to the clean-up of the helium. Helium was chosen as a carrier gas because its ionization potential and the potential of its lowest excited state are higher than those of any other element, and as a consequence the helium will not limit the velocities or energies of the electrons to values too low to excite any test element that might be introduced. As a matter of fact, since these are the highest known, we would expect that the

\* For the entire paper, see R. A. Wolfe and O. S. Duffendack: *The Quantitative Spectrochemical Analysis of Mixtures of Gases*. *Proc., Sixth Summer Conference on Spectroscopy and Its Application*, Massachusetts Institute of Technology (1939) 66-70. Technology Press.



spectrum of any test element would appear in the spectrum of the mixture and that seems to occur. However, it is found that metastable helium atoms react not chemically but energetically with molecules of other gases, and transfer their energies to these molecules, therefore the spectrum of helium is affected. The lines that would be used in the analysis, those that are in the range convenient for spectroscopic recording, involve metastable states of helium, consequently their intensities depend upon the concentration of metastable helium, and the concentration of metastable helium will be affected because of these impacts, as we call them, of the second kind with the molecules of the test element.

J. CHIPMAN.—Suppose the metal contained a little bit of argon, how would that affect the results?

O. S. DUFFENDACK.—If the metal contained argon, I am afraid we could not use the argon then as a standard. Of course a blank test would be necessary first of all to show that the metal contained the argon, which would be extremely unlikely. If the metal contained argon, some other standard would have to be used, probably krypton or xenon. I should have said that analyses of gas mixtures like this can be carried out in about one-half hour.

#### Oxygen Samples from Open-hearth Bath\*

By K. C. McCUTCHEON,† and L. J. RAUTIO‡

The original alumina-residue method, as described by Herty, was to take a spoon sample from the bath and shake off the slag before fully killing with aluminum wire; then skim off the scum and pour the sample into a test box. The reliability of this method and of its various modifications was investigated thoroughly in 1934. The

TABLE 1.—*Results in Alumina-residue Method*  
PERCENTAGES

First Sample		Second Sample		Type of Heat, Percentage of Carbon
FeO	Oxygen	FeO	Oxygen	
0.477	0.106	0.445	0.099	0.04-0.06
0.432	0.096	0.210	0.047	0.04-0.06
0.283	0.063	0.287	0.064	0.08-0.10
0.338	0.075	0.348	0.077	0.04-0.06
0.226	0.050	0.308	0.068	0.04-0.06
0.359	0.080	0.325	0.072	0.04-0.06
0.253	0.056	0.270	0.060	0.04-0.06
0.211	0.047	0.322	0.072	0.04-0.06
0.320	0.071	0.443	0.098	0.04-0.06

data were obtained by carefully taking a series of simultaneous duplicate samples from a number of heats, discarding the samples that showed any reaction whatsoever before or during killing. The results in Table 1 were obtained on duplicate samples taken at tap from low-carbon rimming heats.

\* Paper read before the Ohio Valley Section of the A.I.M.E., Ashland, Ky., Nov. 4, 1937.

† Assistant General Superintendent, Ashland Division, American Rolling Mill Co. Ashland, Ky.

‡ Instructor of Metallurgy, Ohio State University, Columbus, Ohio.



While some of the pairs agree closely, as the third, others are so far apart that no reliance should be placed in the results. Obviously the best technique was not good enough and a better method had to be developed.

#### *New Method*

Since the only sources of error are oxygen from the slag and atmosphere, it was necessary to keep the sample from contact with slag or air, and therefore to kill and partly solidify the sample within the bath. The spoon designed was a small, juglike,

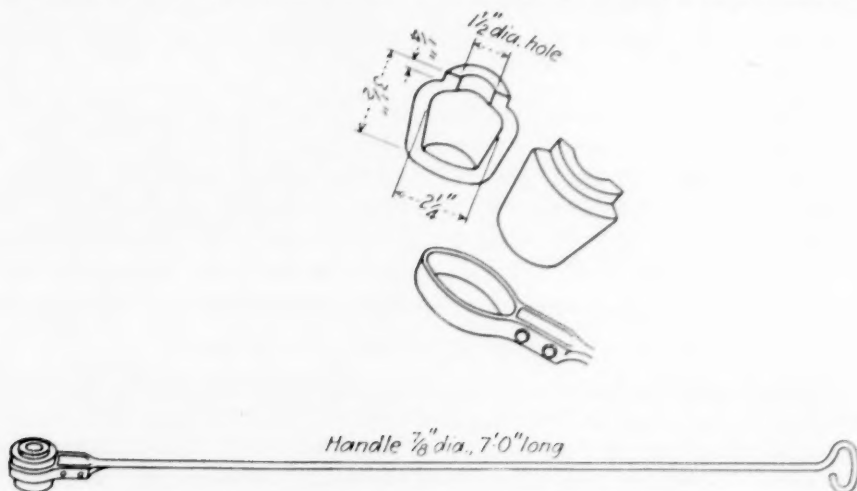


FIG. 1.—TEST SPOON FOR TAKING BATH SAMPLES.

heavy-walled casting, split down the middle and held together by a steel loop attached to a handle (Fig. 1).

#### *Sampling Procedure*

To take a sample weighing 1000 grams, about 5 grams of 0.081-gauge aluminum wire is coiled into the spoon—enough to thoroughly kill the sample. The hole is closed with a light sheet-iron cap, generally a pillbox of 0.010-gauge material. The bottom of the spoon is slagged, care being taken that no slag is splashed on top of the cap. The slagging must be done rather quickly, otherwise the cap might burn through, thereby defeating its purpose of keeping the slag from entering the spoon. The spoon is then pushed into the metal until it no longer has a tendency to float, indicating that the spoon is full.

After it is withdrawn from the furnace the sample is allowed to solidify completely. To release the sample from the mold the hoop is knocked off, permitting the sectional mold to split. Poor samples are detected immediately. Practically the only way to contaminate such a sample is by allowing the cap to burn through, permitting slag to enter and partly cover the sample. After some practice it is possible to take a sample in a very few minutes.

Table 2 shows the results obtained from analysis of simultaneous duplicate samples taken at tap.

All pairs of these samples agree closely in analysis for total oxygen content and indicate that the method is sufficiently reproducible. In addition, the samples have been found to give better results than the ordinary method for carbon, manganese and sulphur.

The need for an enclosed spoon for oxygen samples probably was first pointed out by Schenck, in Europe. The specially designed spoon used by the American Rolling

TABLE 2.—*Analysis of Simultaneous Duplicate Samples Taken at Tap*

First Sample		Second Sample		Type of Heat, Percentage of Carbon
FeO	Oxygen	FeO	Oxygen	
0.226	0.050	0.211	0.047	0.04-0.06
0.235	0.052	0.230	0.051	0.04-0.06
0.211	0.047	0.190	0.042	0.04-0.06
0.186	0.041	0.179	0.040	0.08-0.10
0.213	0.047	0.198	0.044	0.08-0.10
0.213	0.047	0.217	0.048	0.08-0.10
0.103	0.023	0.099	0.022	0.10-0.15
0.114	0.025	0.109	0.024	0.10-0.15
0.175	0.039	0.171	0.038	0.08-0.10
0.310	0.069	0.310	0.069	0.04
0.234	0.052	0.235	0.052	0.04-0.06
0.165	0.037	0.169	0.038	0.08-0.10
0.156	0.035	0.160	0.036	0.08-0.10

Mill Co. embodies the principles recognized by Schenck but was developed independently of his work. It has provided a practical, foolproof way for obtaining oxygen samples, as proved by analysis of simultaneous duplicate samples.

#### Discussion

F. G. NORRIS,\* Steubenville, Ohio.—Is there any advantage of a pillbox over the ordinary top?

J. CHIPMAN.—When McCutcheon and Rautio began, they pounded a piece of tobacco can into the hole to close it, and it answered the purpose. The addition of the pillbox was a slight refinement, which cost the company about one cent extra per sample, or less. It was a little faster to set up.

B. M. LARSEN,† Kearny, N. J.—We tried Mr. Rautio's method with the pill-boxes. It almost invariably gave lower results than the usual spoon-sampling method (an average of 0.04 per cent less). We plan to do some more work on it, but, as with the vacuum-fusion method for oxygen investigation, there seems to be no definite way to be sure of the best method of analysis. There is no check on the absolute level of oxygen. Oxygen of the open-hearth bath apparently is supersaturated and that supersaturation is sensitive to many things.

In taking out the slagged spoon containing metal and pouring into a mold containing aluminum wire, the metal may pick up oxygen from air or slag, but so far our results have not indicated it. The cross checks of various kinds, such as taking out repeated samples, or samples from different parts of the bath, seem to have indicated that the ordinary spoon-sampling method is efficient. For example, taking out a spoon sample and holding it for an increasing number of seconds usually gives the same result until the metal in the spoon begins to freeze, then boiling begins on that frozen metal.

We are still uncertain as to the best method of determining this fugitive supersaturation in the  $(C \times FeO)$  product, but we have seen no definite evidence yet in favor of one or the other method.

\* Metallurgist, Wheeling Steel Corporation.

† Research Laboratory, U. S. Steel Corporation.

We have used two or three methods of putting the mold into the bath itself and there is always a certain amount of boiling. The question is whether there is not some loss of oxygen—some dissipation of the supersaturation—in the metal entering the mold.

J. CHIPMAN.—This whole method of determination of oxygen by precipitation of  $\text{Al}_2\text{O}_3$  was started by Dr. Herty, and I think he has used the bomb. Let me call on him before I call on anybody else.

C. H. HERTY, JR.,\* Bethlehem, Pa.—We took up the bomb test as soon as McCutcheon and Chipman described it. We found one difficulty with it which we think we have overcome—we very often got slag in our bomb, and to avoid that we put on a double cap. We found that to be particularly useful in a test at the last minute when a heat is going out. I do not believe we have had any slag in a test when we used the double cap.

I do not know that I want to admit that my steel was supersaturated with oxygen, but we have found that when we make a plot of the carbon content against the oxygen in the bomb test over the oxygen in the ordinary spoon test, as the original method called for, as the carbon becomes higher this ratio goes down. In other words, with very low carbon and large amounts of oxygen, this ratio approximates 1. At high carbon, where the oxygen content is much lower, there is a spread between the bomb test and the spoon test, indicating that steel that contains a small amount of oxygen picks up more oxygen during the pouring of the spoon test than a steel that is much more closely saturated with oxygen, like low-carbon steel. With a heat around 0.08 or 0.10 carbon, the bomb and spoon will test very closely, but on 0.40 or 0.50 carbon there is a big difference.

We believe the bomb test is by far the most accurate, although at very low carbon the spoon test can be used and not be very much in error. All in all, the bomb test is just as easy to take as the spoon test, and we feel that it is entirely reliable.

W. O. PHILBROOK,† Chicago, Ill.—At the Wisconsin Steel Works we adopted the bomb test for trial the early part of last summer. We went through extensive tests, and had much the same experience that has been reported here.

Plotting oxygen against time, and starting somewhere after the lime boil, our bomb test and spoon test would be similar, perhaps identical. As we went further into the heat, the spoon test would go up rapidly and level off. Say that that represents around 0.17 or 0.18 per cent FeO on the spoon test, and perhaps 0.20 per cent carbon. (These figures are approximate, from memory.) Our bomb test would be much more uniform, gradual in its rise, and at 0.20 per cent carbon there might be anywhere from 4 or 5 to 7 or 8 points difference between the two. So we would get, roughly, at 0.20 per cent carbon, about 0.10 on the bomb test, perhaps 0.17 on the spoon test; then the peculiar thing happened. If we threw in spiegel, as I think Dr. Herty noticed in his original researches, the spoon test would jump. On the bomb sample there would be a very little decrease, perhaps. As the deoxidizers worked through, the bomb test would drop. The spoon test also would drop, so that at the time the bath was killed and the heat was tapped there would be practically no difference between the two.

We also managed to get one bomb test out of the ladle at the platform. The results were very nearly the same as our ordinary spoon test on the platform.

I never satisfied myself as to the reason for the difference between the bomb and the spoon test in an open bath at low carbon. There was a question as to which was correct. We tried to extrapolate  $C \times \text{FeO}$  vs. rate of carbon drop down to zero

\* Research and Development Department, Bethlehem Steel Co.

† Wisconsin Steel Works, International Harvester Co.

carbon drop to get the true equilibrium value, but the extrapolation was not particularly successful and did not give a clear-cut conclusion. However, we have found definitely that there is a much better correlation between carbon and oxygen in the bath all the way from, say, 0.50 carbon down to 0.09 or 0.10 with the bomb test than there is with the spoon test. There may be a difference of 9 or 10 points in different heats with the regular old-fashioned spoon test at the same carbon, whereas with the bomb test the variation probably will not be more than two points. Since we adopted the bomb test we have had 215 heats recorded, all of quality killed steel, and we have plotted a standard curve—an average curve of carbon against FeO as determined by the bomb test—and in 70 to 75 per cent of the cases our routine tests showed that all values were within a range of one point of FeO on either side of the average value.

Following are some values from the average curve:

C, PER CENT	FeO, PER CENT	(C × FeO)
0.10	0.170	0.017
0.15	0.126	0.019
0.20	0.104	0.021
0.30	0.081	0.024
0.40	0.068	0.027
0.50	0.061	0.0305
0.60	0.057	0.034

Of course, according to Dr. Chipman and other recent work, the probable equilibrium value is in the neighborhood of 0.011, at low carbon, and we are somewhat above that, as we still have carbon drop. This value was found some years back by Schenck, who verified that that working constant increases as carbon increases.

We found it better to set the pillbox  $\frac{1}{2}$  in. above the surface of the mold rather than flush, because it melted better. Ordinarily, we do not have trouble with slag in the mold if we are careful in slagging the test bomb. It is necessary to get it slagged and under the surface of the bath as rapidly as possible, to prevent too early melting of the cap or slagging over of the cap.

B. M. LARSEN.—We obtained effects similar to those mentioned; that is, the tendency for the carbon-oxygen product as found in the bath to increase with the increasing carbon. The whole picture indicates the reaction is affected by excess of one of the reagents and not both of them. I just want to reiterate that this question of the choice between these two sampling methods is one of opinion now and not of fact because we have no way of determining the right result.

J. CHIPMAN.—Since Mr. Rautio is not here, I think the one who has used the bomb method the next longest is probably Mr. Frank Norris.

F. G. NORRIS,\* Steubenville, Ohio.—At present the only tests that we can apply are the tests of consistency. We do not know the absolute values, that is, accuracy, but we can come to some judgment as to the precision of the method. You cannot keep people from using an average value. They will take 4 or 20 tests and draw an average curve for each carbon content, so that some 200 tests are summarized into six or eight values. A summary is necessary, but the sampling method should be as precise as the chemical method. By making four determinations, comprising duplicate chemical determinations on drillings from duplicate samples, if the sampling method is as precise as the chemical method, a test of consistency should indicate no assignable cause for variation. If the bath is changing so fast that in a minute or two there is a difference between duplicate determinations, I do not care what the

\* Wheeling Steel Corporation.



values are. For practical purposes we do not have to worry about differences in bath composition between the two duplicate samples. Tests of this nature will take conclusions out of the realm of opinion.

M. W. LIGHTNER,\* Munhall, Pa.—How much time does it take for the two caps to melt? When we began to experiment with this, we did not work fast enough to prevent slag from getting into the sample. We put on a little heavier cap, and found that we were getting lower results than with the lighter cap, probably because we were getting a reaction on the spoon. With the lighter cap and careful sampling there should not be much question of getting slag in the test.

Mr. Norris emphasized the accuracy of the test very well. If you cannot take two tests simultaneously out of the same door and check them within a hundredth of a per cent, there is something wrong with your method.

C. H. HERTY, JR.—We take 6 to 10 sec. after the immersion, but we are careful to slag the bomb very well before we immerse it. I never have seen a boiling on the spoon if the bomb is slagged properly, about halfway up the pillbox. It is thrust down into the bath, held for 7 or 8 sec., and brought right up.

F. G. NORRIS.—If the bomb is slagged over the top of the box, slag gets in the sample, which is unsatisfactory.

L. H. NELSON,† Buffalo, N. Y.—How much effect does the depth have—for instance, if you take a test in the middle door and one in the end door, where there is an appreciable difference in bath depth?

C. H. HERTY, JR.—In an active bath, you get practically the same oxygen from any door; if you kill the heat, there is some variation.

L. H. NELSON.—That would not be true during the lime boil.

C. H. HERTY, JR.—We do not worry much about a test during that period.

B. M. LARSEN.—We had some experience with distribution of the bath. Normally, at least in many furnaces, there is not much difference longitudinally in the top layer of the metal. Samples taken out of different doors check very closely, but if the bath is not boiling violently there is a difference between top and bottom; that is, the bottom of the bath near the hearth is lower in iron oxide than it is near the slag, which it should be, perhaps, from some other indications, and as a check on that, if the bath is boiling violently, this difference between top and bottom is smaller.

W. O. PHILBROOK.—We have found that carbons run on our bomb test will be the same, or as much as three points of carbon on a 40 carbon test higher, than those taken on our regular spoon test for preliminaries, and we are sure that our bomb test is taken deeper, perhaps 10 in. There is definitely higher carbon at that lower depth and probably that explains some of the difference in FeO.

F. G. NORRIS.—In answer to the question of whether there is better agreement from high-carbon tests than from low-carbon tests, it has been our experience that we can get reasonably satisfactory evidence of consistency between the bomb test and the spoon test, each taken in duplicate early in the heat, which is at 0.50 or 0.60 C. At lower carbon, with the spoon test, possibly 7 out of 10 or 8 out of 10 will still remain consistent. The disagreement is at the time when we are most interested in the results, which is the sample before spiegel and during the interval between spiegel

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† Assistant Superintendent, Open Hearth Dept., Republic Steel Corporation.



and tap. The bomb test has evidence of higher consistency for a greater percentage of the time than does the spoon test. Late in the heat the spoon test will check a good portion of the time, but once in a while it will be in error. When we can take only one sample, which we have to do as a matter of routine, the bomb test is preferred. Early in the heat the two methods are practically interchangeable.

#### Rapid Analysis of Sample for Alumina

B. M. LARSEN.—We have been using turbidity in the Corporation for several years. The sample in solution is placed in a tube and the variation in turbidity caused by the aluminous suspension is measured. Recently we have improved this method a little, so now we feel that it is accurate to within about 0.01–0.02 per cent FeO. That enables us to regard differences between different samples of 0.02 per cent FeO as significant in most cases, and it is really of some use to have it so accurate. Apparently the turbidity method can be made more accurate than an ordinary analytical method, because normally there are inaccuracies in the analytical determination of aluminum unless a good deal of time is spent on it. An ordinary analytical determination does not go down to 0.01 per cent FeO. The time required by the turbidity method is very short once the solution is prepared, the total time for analysis being 15 min. or less.

A. B. KINZEL,\* New York, N. Y.—A few years ago we published a paper† on a method using graphite to bring down the alumina in a centrifuge and thus shorten the time of the operation. The sampling problem was acute at that time, but it seems that with the present satisfactory sampling it would be worth while to take another look at the rapid analytical method.

#### Accurate Carbon Analyses in Low-carbon Steel

J. CHIPMAN.—The method of determining oxygen is becoming sufficiently consistent now so that we are wondering if the method for determination of carbon is sufficiently accurate and sensitive to give the best values for carbon-oxygen products and as a means for studying the important reaction between carbon and iron oxide.

I am going to call first on Prof. T. L. Joseph.

T. L. JOSEPH,‡ Minneapolis, Minn.—The use of barium hydrate in determining carbon in steel is well known. The principle involved is that the carbon dioxide ordinarily absorbed in ascarite is absorbed in a solution of barium hydrate. It is necessary, of course, to maintain an excess of barium hydrate in this solution to be sure of obtaining efficient absorption. This excess of barium hydrate is then determined by titrating with hydrochloric acid.

I am not offering a new method,§ but shall describe certain refinements in adapting this volumetric method to determining carbon in the low-carbon range.

Fig. 1 shows an ordinary combustion carbon outfit. An ascarite tube, *B*, absorbs any carbon dioxide before the oxygen enters the furnace. There is a slight innovation at the inlet end of the tube. To get accurate results we had to eliminate the rubber stopper on the inlet end. The contact is made on the outside by means of

\* Chief Metallurgist, Union Carbide and Carbon Research Laboratories.

† Kinzel, Egan and Price: Rapid Determination of Oxide in Molten Steel. *Metals and Alloys* (March 1934).

‡ Professor of Metallurgy, Minnesota School of Mines and Metallurgy.

§ A paper describing this method was published in *Blast Furnace and Steel Plant* (1939) 27, 347–351, with M. H. Kalina.

a rubber band and funnel-shaped glass tube that prevents contamination from the rubber stopper (Fig. 3). The sample is held in the ordinary alundum boat. Asbestos fiber and broken quartz were placed in the end of the tube to cut down the volume. The carbon dioxide and oxygen leave the tube and enter an absorption tower *F*, which contains a standard solution of barium hydrate. This solution can

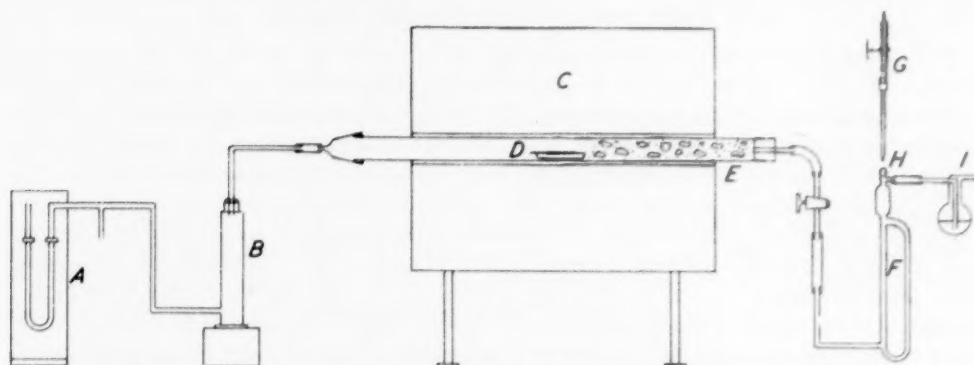


FIG. 1.—APPARATUS FOR VOLUMETRIC DETERMINATION OF CARBON.

*A*, manometer tube.  
*B*, ascarite tower.  
*C*, furnace.  
*D*, sample boat.  
*E*, quartz and asbestos.

*F*, CO<sub>2</sub> absorption tower.  
*G*, micropipette.  
*H*, rubber stopper.  
*I*, CO<sub>2</sub> detector.

be expressed in units of carbon. The construction of the absorbing tower causes a continual circulation of the liquid in the tower; the liquid rises in the left-hand vertical arm and moves downward in the right-hand vertical arm. This circulation is very desirable because the titration can be conducted right in the absorption tower.

TABLE 1.—Comparison of Carbon Determinations on Steel Ranging from 0.03 to 0.1 Per Cent Carbon

Sample		Previous Analysis		Analysis (New Method), C, Per Cent	Variation from Mean, C, Per Cent
Source	No.	Analyst	C, Per Cent		
Bureau of Standards	15b	Bureau of Standards	0.101	0.1028	+0.0018
	15b		0.101	0.1003	-0.0007
	15b		0.101	0.1007	-0.0003
	15b		0.101	0.1016	+0.0006
	15b		0.101	0.1023	+0.0013
	15b		0.101	0.1008	-0.0002
	15b		0.101	0.0997	-0.0013

Above the absorption tower is a small titrating pipette, which I will describe later. The procedure after the blank determination has been made would be to start the gases moving through the absorption tower and as the gases are evolved the alkalinity or the strength of the barium hydrate solution decreases. After about 10 min., the combustion is complete. The small titrating pipette (Fig. 4) is then moved down

through the opening containing stopper *H* and the tip is placed in the liquid. It is important to do that, otherwise there will be errors due to drop effects. A small bulb, *I*, simply detects any carbon dioxide that might not be absorbed.

Fig. 2 shows the absorption tower. When the gases enter the lower left-hand arm, some liquid is displaced and the gases rise into the capillary tube on the left and act as a sort of air lift, so that the liquid in the tower circulates, thus increasing the speed of the titrations. The enlarged portions of the tube facilitate absorption.

One of the difficulties encountered was to develop a means for introducing into the absorption tower a definite and reproducible amount of barium hydrate. The automatic-leveling, constant-delivery micropipette shown in Fig. 3 was made out of a piece of capillary tubing, drawn to a tip at one end, with a small piece of rubber tubing placed at the top. By manipulating this rubber tube the liquid is drawn up into the bulb above the constriction and then is allowed to flow out. When it reaches the constriction, surface tension is sufficient to prevent any further movement of the liquid in the

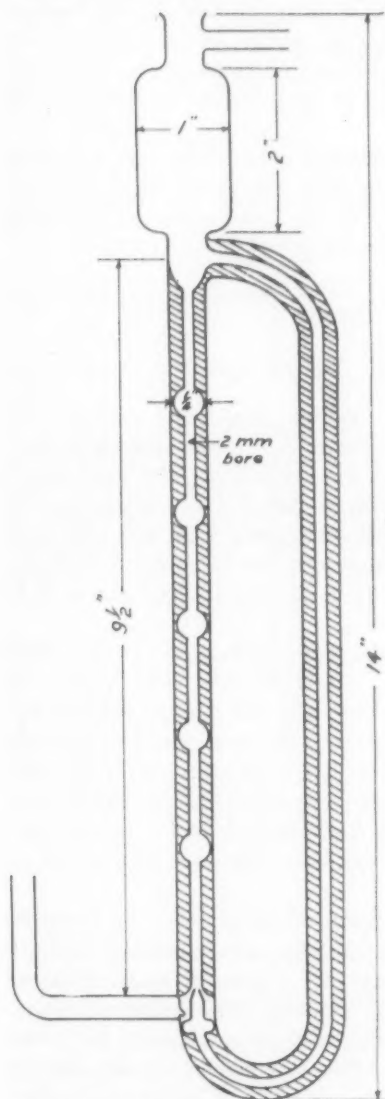
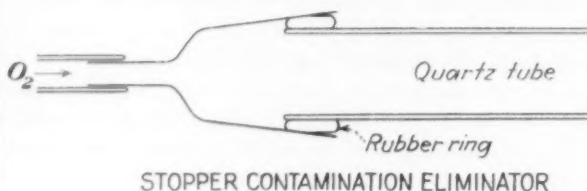


FIG. 2.—Tower for absorbing carbon dioxide.



STOPPER CONTAMINATION ELIMINATOR

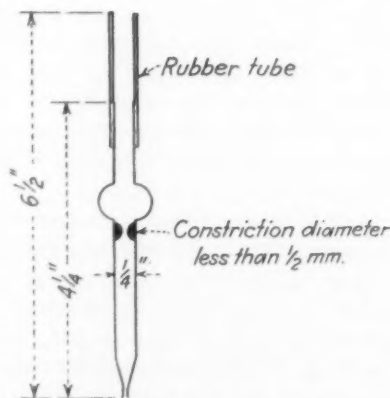


FIG. 3.—Constant delivery pipette and inlet connection to combustion tube.

capillary tube, so that, time after time, a definite quantity of the standard solution can be obtained for adding to the absorption tower. By taking 20 of these pipettes and determining the strength of the barium hydrate solution by precipitation of barium sulphate, we were able to standardize the solution that is used in the absorption tower.

Fig. 4 shows the small capillary pipette used to back titrate with hydrochloric acid. The drawing shows a rubber tube closed at one end. An ordinary screw clamp with some metal arms attached to the jaws fits around the rubber tube, and by means of this pinch clamp the discharge from the pipette can be controlled very carefully. A piece of calibrated wax paper is placed on the back of the pipette to get a measure of the solution discharge.

Fig. 5 shows a dispenser designed to prevent contamination of the barium hydroxide by carbon dioxide in the atmosphere. Air flows through the ascarite bulb and forces the solution up into the chamber *D*. The constant-delivery pipette is then inserted into the chamber *D* and a known amount of the solution is removed and transferred to the absorption tower.

In Table 1 are some results on Bureau of Standards sample 15-*b*, with a carbon content of 0.101. The results by this method are rather consistent; variations are on the order of one thousandth per cent of carbon. Close checks were obtained on many other steels of even lower carbon contents (0.03 to 0.08 per cent C).

#### LABORATORY TECHNIQUE FOR STUDY OF REACTIONS INVOLVING LIQUID METAL

Dr. T. L. Joseph took the chair. B. M. Larsen opened the subject as follows:

B. M. LARSEN.—The study of slag-metal-gas systems and their equilibria is burdened with difficulties of technique essentially because: (1) the extremely high temperature level of around 1600°C. so limits the available materials and makes isolation of the system so difficult on account of extreme temperature gradients; (2) slags containing iron oxide are very corrosive to all substances that will also hold liquid metal; and (3) the oxygen pressures at equilibrium with liquid iron are extremely low, introducing the necessity of either substantially removing the gas phase or of making it neutral to the slag-metal combination.

In the metal phase, the biggest puzzle is to explain the mechanism of the C-FeO reaction with its tendency toward supersaturation. The reaction rate appears to depend on the excess, not of both reagents but essentially only upon that of the FeO. Even this excess does not relate itself well to the reaction rate but appears to be affected mainly by such factors as the amount of agitation, contact with solid surfaces, etc. Oelson and Körber, in Germany, have introduced carbon into melts in silica crucibles and thrown some light on the reaction, but it needs more laboratory study to correlate with those made under less controlled conditions in large steelmaking furnaces.

For the slag-metal reactions, we are most seriously in need of more data on the compounds in liquid steelmaking slags. Phase diagrams will help a little, but not only are actual mixtures too complicated but we learn nothing very definite from them about what is present in the liquid state. We can attack the problem from slag-metal melts, obtaining distributions of Mn, S or FeO with varying slag composition. Here the problem is essentially that of suitable containers. We can either try to develop refractory crucibles almost unattacked by the slags or we can limit our slag mixtures to compositions essentially saturated with the crucible material, as Körber and associates have done in the Fe-Mn-Si-O system, using only slags saturated with SiO<sub>2</sub>. The use of rotating crucibles in which the liquid metal is the container for the slag is a big step forward in this field.

By heating slags in platinum crucibles in controlled oxygen-pressure atmospheres, studying the change in the ratio of FeO and Fe<sub>2</sub>O<sub>3</sub> with varying oxygen pressures and varying slag composition, we can approach within reasonable extrapolation distance from the oxygen-pressure levels in steel baths. This method is particularly adaptable

to open-hearth slags, which are in practice in contact with metal underneath at an extremely low oxygen pressure and to a gas phase above with this pressure some hundred million times higher. It has been used with some success in our laboratory, and will be discussed briefly by Dr. Darken.

I believe Mr. Sims, of Battelle Laboratories, used a similar method of studying the deoxidization equilibrium by defining the equilibrium with the oxygen pressure of the gas phase. This is one method of controlling the system without the necessity of having a crucible with the slag and metal present together.

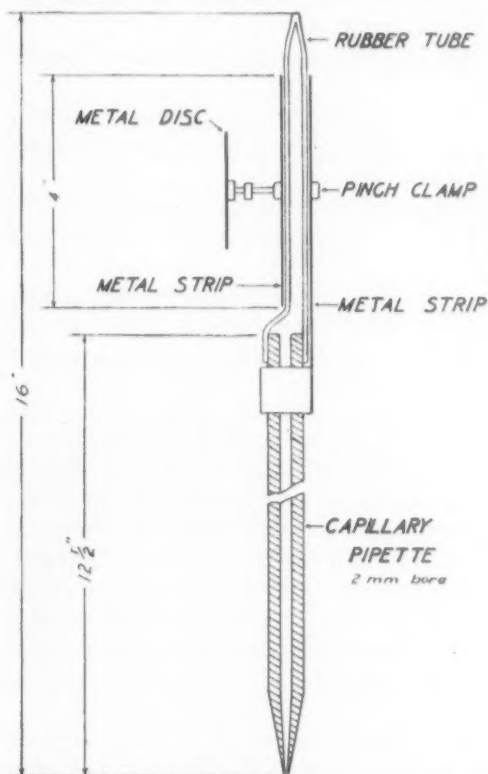


FIG. 4.—TITRATING PIPETTE AND CONTROL.

### Rotating Liquid Crucibles

E. P. BARRETT,\* Minneapolis, Minn. When a vessel containing a liquid is rotated, the inner surface of the liquid takes the shape of a paraboloid, under

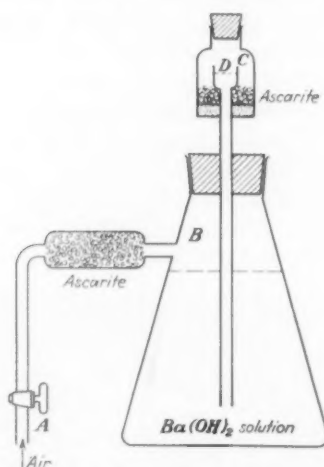


FIG. 5.—APPARATUS FOR STORING STANDARD SOLUTION OF BARIUM HYDROXIDE.

the simultaneous action of centrifugal force and gravity. The internal dimensions of the paraboloid are governed by the diameter of the surface of the liquid and its speed of rotation.

Three high-frequency induction laboratory furnaces, using rotating liquid metal crucibles, were designed and constructed by the Blast Furnace Studies section of the Metallurgical Division of the Bureau of Mines for the study of slag-metal reactions.<sup>1</sup> This apparatus is especially suited for the study of slag-metal reactions because it affords a means for holding molten slag in contact with only the liquid metal forming the rotating crucible. Two of these furnaces at the Bureau of Mines in Minneapolis and one constructed in cooperation with the Metallurgy Department of the School of

\* U. S. Bureau of Mines.

<sup>1</sup> E. P. Barrett, W. F. Holbrook and C. E. Wood: Induction Furnaces for Rotating Liquid Crucibles. *Trans. A.I.M.E.* (1929) **135**, 73.



Mines, University of Minnesota, are being used in studies of slag-metal reactions. I believe that the results being obtained could not have been obtained in other types of apparatus. In operation:

1. The refractory crucible must be centered with respect to its axis or rotation;
2. With rotation stopped, the metal charge is placed in the refractory crucible;
3. The cover is attached to the furnace;
4. The flow of nitrogen is adjusted to produce a slight pressure within the box inclosing the furnace;
5. The charge is heated slowly to red heat and then the power increased to melt the metal;

6. When the metal is liquid, rotation may be started. The speed of rotation varies with the diameter of the refractory container and the height of liquid crucible desired. Do not use a higher crucible than necessary.

7. The temperature of the liquid crucible may be determined by sighting with an optical pyrometer through a glass window fitted in the observation tube attached to the cover of the furnace.

8. When the desired temperature has been attained, slag or slag-forming materials in the form of briquettes may be introduced into the rotating liquid crucible through the tee in the observation tube. The briquettes must not contain moisture or carbon dioxide. Materials that react to evolve gas should be added in small quantities.

9. When the slag has been in contact with the metal for the predetermined time at the desired temperature it is readily removed upon removal of the furnace top by touching the slag with a cold copper-tipped rod, which causes the slag to solidify almost instantly, thus preventing changes in composition that might occur upon slow cooling. I use a copper tip about 1 in. in diameter by 6 in. long on a  $\frac{5}{16}$ -in. Nichrome rod. The end of the copper tip has a shoulder  $\frac{1}{2}$  in. long by  $\frac{1}{2}$  in. in diameter, with a projection  $\frac{1}{4}$  in. long by  $\frac{1}{4}$  in. in diameter on its lower end. This shape causes the chilled slag to adhere readily to the end of the copper tip. The copper tip is cooled in water between contacts with the liquid slag. Rotation of the liquid crucible must be maintained until a sample or all of the slag has been removed. The metal may be sampled by chilling a portion on an iron rod.

10. If the metal remaining in the furnace is of a composition that may be used for another test, the furnace cover is replaced, the temperature adjusted and more slag or slag-forming materials added as in step 8.

Type 3,<sup>2</sup> in which the entire furnace rotates, seems to have the greatest possibilities. Preformed refractory crucibles may be centered within the coil by means of a jig and packed in powdered refractory for heat insulation. Some of the advantages are:

1. Larger charges may be used.
2. Better coupling is afforded between coil and charge.
3. The refractory crucible backed up with refractory powder is stronger than the crucible alone. It is colder than the metal charge, and a crack in the crucible is not likely to cause loss of the metal and failure of the test.
4. The fact that the refractory is colder than the metal, especially above the upper line of contact with the metal, suggests a method of operation with slags of such composition that they wet the surface of the metal and tend to climb out of the rotating liquid metal crucible. I believe that the slag that climbs over the top of the metal will solidify on the colder refractory and form a barrier, which will hold further additions of slag within the rotating liquid metal crucible. Inasmuch as the barrier is the same composition as the slag being studied, there will be no contamination of the molten slag within the metal crucible.

<sup>2</sup> *Trans. A.I.M.E.* (1939) **135**, 81.

*Vacuum-type Furnaces*

Vacuum-type furnaces for rotating liquid metal crucibles are possible and present no extremely difficult problem in construction. Proper design and careful construction are essential to the successful operation of laboratory high-frequency induction furnaces using liquid metal crucibles for the study of slag-metal reactions.

*Laboratory Refractories for Liquid Metals*

Laboratory refractory crucibles for liquid metals are of great importance to all research workers conducting investigations at high temperatures. A very simple method for preparing laboratory refractory crucibles was developed by Barrett and Holbrook,<sup>3</sup> in which dry refractory material is packed in a graphite mold by means of an electric vibrator.

This method of forming crucibles may be used with refractories other than fused magnesia. Excellent crucibles have been prepared from Alundum X minus 100 mesh, fired to 1700°C. in the induction furnace. These crucibles were used as containers for liquid iron crucibles rotated 280 r.p.m. for 1 to 4 hr. at temperatures of 1560° to 1725°C. Purified fused alumina and zirconium silicate have been used also to form laboratory refractory crucibles for liquid iron.

*Discussion*

J. G. THOMPSON,\* Washington, D. C.—Our particular interest in refractories has been for melting high-purity metal, particularly high-purity iron. In our experience we still have to find the ideal refractory. Silica is objectionable; likewise slight traces of sulphur are bad and exceedingly hard to eliminate. Magnesia, as has been mentioned before, is somewhat volatile and tends to be reduced at temperatures that are employed in melting iron and steel. The best refractory that we have encountered recently is beryllium oxide, which is useful up to at least 2000° C., is practically immune to carburization, and on the whole is quite satisfactory.

*Stationary Crucibles*

E. R. JETTE,† New York, N. Y.—A furnace was built a few years ago in the Research Laboratories of the American Rolling Mill Co. for studying slag-metal

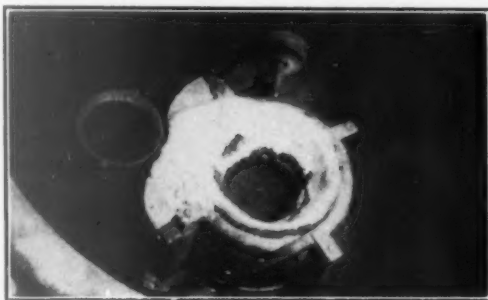


FIG. 1.—INTERIOR VIEW OF FURNACE FOR SLAG-METAL EQUILIBRIUM STUDIES.

reactions. Fig. 1 shows the general structure of the induction furnace. The coil is 7 in. in diameter and is mounted as shown on trunnions through which power and water leads enter. The heavy copper mold is placed so that when the furnace coil is tipped the entire charge of metal and slag runs into it and is rapidly solidified. Into the furnace coil is built a crucible of sintered magnesium oxide, which is conditioned by melting in it a charge of pig iron, raising the temperature to about 3000°F. before pouring out the charge. In actual runs with slag present a considerable amount of the slag is soaked up, especially during the first runs.

<sup>3</sup> E. P. Barrett and W. F. Holbrook: An Improved Method for Forming Fused Magnesia Crucibles. *Ind. and Eng. Chem., Anal. Ed.* (Feb. 15, 1938) 91-93.

\* National Bureau of Standards.

† Associate Professor of Metallurgy, School of Mines, Columbia University.

In order to control the atmosphere, the coil and mold assembly were placed inside a large container. The first container was made of asbestos board of the Transite type. It was found that during a run a considerable amount of water was liberated from the board and condensed on the cold coils. After the walls cooled they would slowly absorb moisture from the laboratory atmosphere and by the time the next run was started the moisture content was about the same as before. For this reason large tile was adopted. Even when the tile was used water vapor was never completely

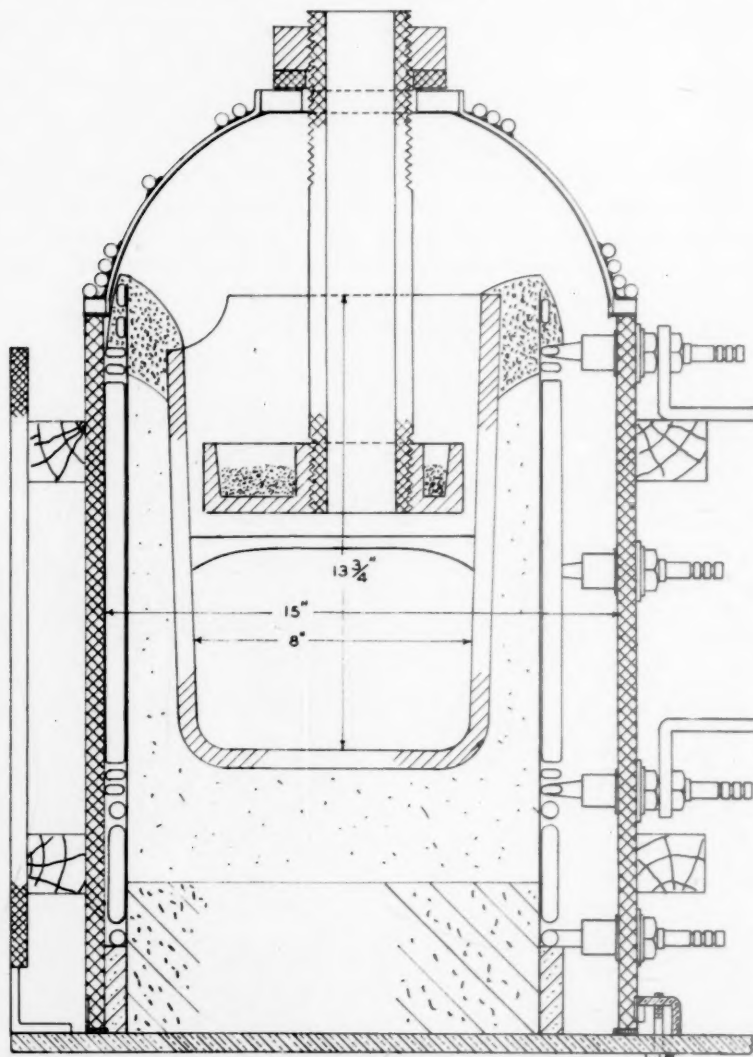


FIG. 2.—VACUUM-INDUCTION FURNACE.

eliminated, although it was considerably less than before. The sources were presumably: (1) the refractories on which the assembly rested, (2) the patches in the crucible lining, although these were heated for a considerable period before the run and (3) organic material, such as Bakelite, used in the coil structure, which frequently was charred. The effect of water vapor on the slag composition was minimized to a certain extent by the flow of dry, oxygen-free nitrogen, which entered the furnace through the center of the graphite heater block directly above the slag layer.

The graphite heater block, inside the high-frequency coil, was used to bring the slag temperature up to that of the metal. It was not, however, possible to measure the temperature of this block under conditions that were strictly comparable to the measurement of the slag temperature.

With this arrangement it was necessary to measure the temperature of the slag by means of an optical pyrometer sighted through the nitrogen-inlet tube and a hole in the graphite block. Corrections for the cooling effect of the nitrogen stream could be made and smoke could be fairly well eliminated. At the time of performing the experiments, it was believed that the temperatures of the graphite, slag and metal were essentially the same. From experience with Dr. Chipman's new equipment at the Massachusetts Institute of Technology, we now question this, and further experiments will be made in an attempt to check the original work.

J. CHIPMAN.—Fig. 2 shows a furnace recently put into operation at the Massachusetts Institute of Technology. The crucible is about 8 in. in diameter and the charge is something like 70 lb. The bath is sampled by dipping in from the top with a small cup, and it is possible to take many samples during the course of a heat by adding iron and slag materials; then it is possible to study in the course of one heat a considerable range of slag and metal composition.

This furnace was built as a vacuum furnace. The shell or vacuum enclosure is outside of the induction coil. It is a Micarta cylinder, which has proved itself to be quite vacuum tight, with a vacuum cover on top. The gadget that goes down from the cover to a level just above the bath is a graphite disk, which is heated by induction to a temperature approximately that of the metal; it is reinforced by some molybdenum wires wrapped around and around in a groove in the graphite. These wires heat better than graphite itself, so it really reaches metal temperature.

Temperatures are measured by inserting a thermocouple from the top right into the metal itself, and no reliance is placed here upon optical determinations of temperature.

The purpose of the vacuum is not to make a steel in vacuum—not to carry out the investigation in vacuum—but to prepare the metal by vacuum treatment to remove all of the gases and to take the carbon content down to below five thousandths per cent, so that samples dipped from the metal solidify with no evolution of gas, and there is, therefore, no loss in oxygen content. The crucible is magnesia, and the slags are essentially saturated with magnesium oxide; i.e., they contain 7 or 8 per cent MgO, which is comparable to open-hearth slags.

The furnace is operated by a 60-kw. motor generator at a frequency of 2000 cycles.

L. S. DARKEN,\* Kearny, N. J.—In order to obtain a clearer insight into the effect of the slag FeO on the carbon-oxygen reaction in the open hearth, our laboratory is conducting an investigation of the system FeO-Fe<sub>2</sub>O<sub>3</sub> and other systems containing these two components. The method consists of holding the sample in a furnace at the desired temperature and in an atmosphere providing a known oxygen pressure until equilibrium is attained; the sample is then quenched in mercury and analyzed. The temperature range covered is from the vicinity of 1200° to 1630°C. The range of oxygen pressures covered is the range between the oxygen pressure in equilibrium with metallic iron and one atmosphere.

Information obtained in this way leads (1) to the establishment of phase diagrams that cannot be reliably determined by other means and (2) to the determination of thermodynamic properties such as activities of the oxides of iron, heats of reaction, heats of fusion, and so forth.

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\* Research Laboratory, U. S. Steel Corporation.



A knowledge of the activity of the oxides of iron in open-hearth slags and the effect thereon of slag composition will, it is hoped, shed some light on the complex phenomenon of oxygen transfer in the open-hearth furnace.

### Jones and Laughlin Experimental Furnace

H. W. GRAHAM,\* Pittsburgh, Pa.—For some 10 years we have been inclined toward the view that the laboratory man has a very easy job of it, that any reasonably intelligent man can generate ideas at a rate that renders useful assimilation impossible. Plant methods, of course have much wrong with them. Present a laboratory idea to a plant man; he tries it at two-thirty some Tuesday afternoon and by a quarter to three he has decided that it will not work. The idea is crushed for all time and cannot be resuscitated. In attempting to meet this situation, we have begun to work on a pilot-scale operation between the laboratory and the mill. The pilot idea is not original with us; it is used in other industries. We have partly completed our original plans and there is one item that may be of particular interest to you, which we can show you now as a moving picture. Dr. H. K. Work, who has charge of our laboratory, will make the running comments.

[Colored motion pictures were shown by Dr. Work. The experimental open hearth has been described in some detail in a paper by H. K. Work and M. H. Banta, published in the 1939 Open-Hearth *Proceedings*, page 161.]

EDITOR.—In response to questions, Dr. Work said that the furnace is fired with natural gas, although it *can* be fired with by-product gas. A cold charge is used, and a preheat in the air of about 1200°, which gives a roof temperature of about 3000°.

H. K. WORK.—On the advice of our plant people the furnace is considerably larger than we originally planned, but that proved to be very fortunate because it allowed us to make the larger heats. The men running the furnace are mill melters and metallurgists.

The furnace has a single door. Originally the door was dry, but the men found it difficult to work around the furnace so a water-cooled door was put in. The standard thickness of the walls is 13½ in. The bath runs about 18 in. The furnace is not insulated, and generally 5 to 6 hr. is required to make a heat; with the larger heats, of course, a little longer. We have made 161 heats in a six-months campaign recently finished. Much of the steel was finished in our mills into various products and is now under investigation.

Most of the material used for operating the furnace is very carefully selected and controlled so that we know accurately what goes into the furnace. When we started we needed experience in operating the furnace, so most of our work was in connection with the analysis of the steels. More recently we have been studying the steelmaking process itself. A great deal of our steel has not yet been tested, and it will be some time before we know exactly what our results are.

We think this method of taking colored moving pictures offers an excellent way of getting a record of what goes on in many of the steelmaking operations being studied on an experimental basis.

To a large extent the work we have done so far has followed our mill practice. As we have gradually gained in experience we have drifted away from that practice and made changes to try out things that we especially wanted to investigate. We have not yet used what might be called slag-control methods, for two reasons: (1) we have a very accurate control over the material for going in, and (2) the changes in the furnace are rather rapid and the making of small additions rapidly is difficult. I think the latter can be worked out, but we have not yet done anything about it.

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\* General Metallurgist, Jones and Laughlin Steel Corporation.



We have been more than pleased with the results we have been getting from the furnace. There is a psychological advantage in talking with mill people when experiments are made under conditions reasonably close to mill conditions, and we feel that we are succeeding in bridging the gap between laboratory work and mill work that Mr. Graham mentioned.

MEMBER.—How big is the nozzle opening?

H. K. WORK.—It is about  $1\frac{3}{4}$  in. Smaller nozzles froze.

MEMBER.—What is the temperature loss of the ladle?

H. K. WORK.—We have not been able to take the time to determine the temperature.

MEMBER.—Do you obtain ladle skulls?

H. K. WORK.—Yes, we usually have a ladle skull of 80 to 100 pounds.

### Vacuum Melting

A. D. MEYER,\* Trenton, N. J.—We have recently built two high-frequency furnaces, for export, designed to melt and pour at partial pressures. Fig. 1 (p. 150) shows a 50-lb. furnace. The case is welded steel and a projection at the bottom contains the mold. This furnace is operated from a 2000-cycle generator, 100 kw., and melts in 15 or 16 min.—a little too much power for proper melting. The top is water-cooled but the mold projection is not, as it does not get hot. The gaskets are of rubber. The side walls run about 100°C. without water cooling. We stay about 8 in. away from the steel. Since this furnace was going abroad, we decided to water-cool the shell and keep it down to room temperature, to be perfectly safe.

The power loss in the furnace shell is 2 kw. We were able to obtain a vacuum of 1 mm., and as we went through the melting point the pressure at the highest point was about 3 mm. Two or three minutes later it dropped back to the 1 mm. mentioned before.

### MEASUREMENT OF TEMPERATURE OF LIQUID IRON AND STEEL

T. S. Washburn, Metallurgist with the Inland Steel Co., Indiana Harbor, Ind., was in the chair at the opening of the afternoon session.

### Pouring and Teeming Temperatures

L. H. NELSON,† Buffalo, N. Y.—The optical pyrometer has done a reasonably good job during the past years in measuring the pouring and teeming temperatures, when precautions are used in making readings. When you are careful not to read through much fume and smoke and have a fairly clear stream to sight on you can usually check results within 10° to 15°F., and this is accurate enough for open-hearth operating control.

One thing I have experienced with the optical pyrometer, however, is that it is not always possible to compare temperatures obtained in one plant with those obtained in another plant, even by using the same type of pyrometer. This difference from plant to plant seems to be more pronounced in measuring rolling temperatures than in measuring liquid-steel temperatures.

Now that many open-hearth furnaces are equipped with temperature and combustion control, the most pressing demand of the open hearth on technical knowledge is for

\* Ajax Electrothermic Corporation.

† Assistant Superintendent, Open Hearth Department, Republic Steel Corporation.

reliable and accurate method of measuring *bath temperatures*. Portable optical pyrometers, in my experience, have been found wanting in measuring bath temperatures.

*Spoon Test.*—A test spoon is well slagged and a sample of steel dipped from the bath and poured out slowly. The amount of frozen steel remaining in the spoon indicates temperature. In my experience, the spoon test will tell when a bath is definitely cold but not much else.

*Rod Test.*—A rod of given carbon content is immersed in the bath and moved slowly back and forth in a nearly horizontal plane. The shape of the cut on the end of

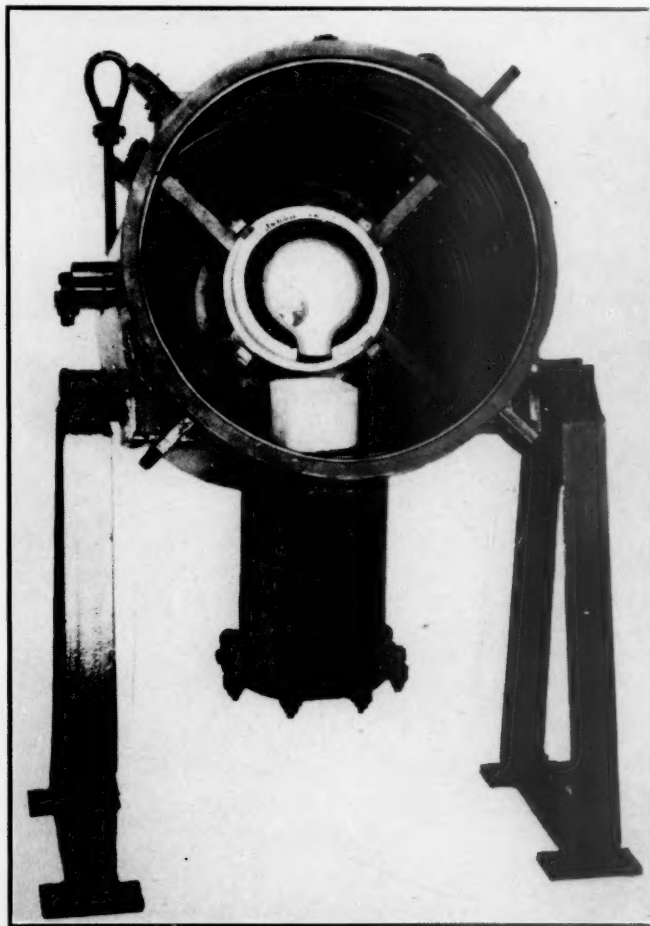


FIG. 1.—HIGH-FREQUENCY FURNACE BUILT BY AJAX ELECTROTHERMIC CORPORATION.

the rod indicates the relative temperature of the bath. Time of immersing rod and viscosity of slag must also be considered. In a very cold bath, the rod collects steel; in a cold bath, it cuts off to a long point; in a slightly cold bath, it cuts off to a short point; in a hot bath, it cuts off square and in a very hot bath it cuts off square or concave and nicks in the slag area. In competent hands, this is still the most reliable practical test of bath temperature.

*Skulling Test.*—A test spoon is well slagged and a sample free of slag is dipped from the bath. The time (taken in seconds with a stop watch) for the sample to skull over the top surface is used as a measure of bath temperature. In my experience, this test is more reliable for the electric furnace with a dead bath than for the open hearth.

**Rod Boil Test.**—A rod is immersed in a bath of steel and causes a boil. If the boil is large enough to expose liquid metal, the temperature is measured by sighting an optical pyrometer upon the exposed metal. The chief difficulty with this test is that often the boil on a rod is not violent enough to expose metal through slags of the viscosity that we wish to work with. Also, producing boils in the bath tends to chill the metal.

**Thermocouple.**—The Fitterer thermocouple has been used to some extent in measuring bath temperatures but I have not had experience with it. The Fitterer couple is a carbon-silicon carbide couple in which the silicon carbide forms the sheath. Some of its disadvantages are short life, long time to make accurate reading, and lack of mobility.

**Pipe Test.**—A pipe is inserted through the bath and temperature is measured by sighting an optical pyrometer down through the pipe to the exposed metal. I have had no experience with this test but would consider it rather dangerous from a safety standpoint.

J. T. MACKENZIE,\* Birmingham, Ala.—We have made some comparative tests with the Bioptix. The instrument is arranged to read both brightness and color. It is delicate and slow. There are two scales. First the brightness is adjusted, then the color, and that throws the brightness off, so it is necessary to work with these two scales until they are together.

Mr. Roeser, of the National Bureau of Standards, checked the instrument and came to the conclusion that its accuracy was about 14°C. under laboratory conditions. The only place we could get to read the instrument was on a large forehearth, where the time of pouring was long enough to make these adjustments. We had two sets of readings on cast iron. With 2540 on the thermocouple, the Bioptix ranged from 2530 to 2550 in four observations, and the L. and N., using the calibration that we have established at Acipco, read 2580 to 2600. Of course, that is the range where the correction is so indeterminate. The stream of iron right in that range may vary from 0.35 to 0.90 emissivity.

We took it over to Tennessee Coal, Iron and R. R. Co. and got some checks on the open hearth against the Leeds and Northrup instrument there, with the following results:

Instrument	Slag	Roof	Steel 1	Steel 2
Bioptix: color.....	3000	2960	2900	2790
Brightness.....	2940		2600	2520
L. and N.....	2990	2940	2947	2875

On the last set of readings smoke and steam were bad, so while the man with the optical could get around and dodge the fumes, the Bioptix reader could not. The instrument was too slow to do that.

#### Bath Temperatures

R. B. SOSMAN,† Kearny, N. J.—We spent some time in 1936 comparing methods of open-hearth bath pyrometry at the Pencoyd plant at Philadelphia. Before speaking of the method we are now using, I want to mention one of the methods we tried there which perhaps will not receive other mention in this session. That was Larsen and

\* American Cast Iron Pipe Co.

† Research Laboratory, U. S. Steel Corporation.

Shenk's so-called "equalization method."\* A roof-control pyrometer is sighted on the inside of the roof, and another pyrometer of the same type is sighted through the roof down onto the slag. If the flame is shut off during the latter part of the heat, the temperature equalizes itself rapidly by radiation, and in the course of a few seconds, or perhaps half a minute, there results a completely uniform temperature in the furnace. If the slag is not in a condition to make it an insulator, it will assume the temperature of the steel because the mass of the steel is so much greater than that of the slag. Consequently roof, slag, and steel all come to the same temperature. If then you have some automatic method of reading the temperature at the moment when the two pyrometers read alike, you have a measure of the temperature of the steel bath.

The pyrometers used were photoelectric. They were connected in opposition through a relay, and when the two became equal within a set range, the fuel would be turned on automatically, producing a mark on the record, which showed just what the temperature was when equalization was attained.

The method you are perhaps more interested in now is the Collins-Oseland tube method (U. S. Patent No. 2020019, Nov. 5, 1935). An open pipe is inserted through the wicket of a door, and air is sent down through the pipe. The outer end of the pipe is closed with a glass window. The air, bubbling up through the bath, maintains a clean steel surface visible through the window in the pipe. Then with an optical pyrometer the temperature of the steel can be read. The apparent emissivity is not the same as from a flat open surface, and the pyrometer must therefore be independently calibrated.

Our development of this instrument has been in the direction of making it automatic by means of the self-generative photoelectric cell. It can be calibrated either in terms of the tapping and pouring temperatures of the steel, read optically, or more satisfactorily by the method of reading the true temperature of the bath with platinum thermocouples.

One of the most sensible things said this morning I think was by Mr. Norris to the effect that a method like this should be studied as to its consistency. We already have evidence of dependability of the method in this, that the pyrometer gives consistent results compared with the operator's knowledge and experience of such baths, while the readings are much more precise than those obtained by any other method except the thermocouple.

L. H. NELSON.—How much effect has the variation in the amount of air used, or how closely do you have to control the air run through the tube?

R. B. SOSMAN.—That does not have any very large effect. There must, of course, be air enough to keep the steel from running up into the tube, and not so much that there is a great fountain of steel inside the furnace, but there is no variation of the apparent temperature with small variations in the air pressure. The use of nitrogen gives a different result, presumably because there is some reaction with oxygen on the surface of the liquid steel.

M. F. YAROSKY, † Chicago, Ill.—Our experience at South Works with an improved bath-temperature pyrometer developed by the Kearny Laboratory is approximately of 8 or 9 months duration. The progress was slow until the emissivity factor was established. However, from that time on bath-temperature readings have been taken consistently, every day, on a number of heats. While we still consider this development to be in the experimental stage, in our opinion it offers most promising possibilities. Although we get occasional erratic results, the majority of the readings

\* *Instruments* (1940) **13**, 127-130.

† Assistant Division Superintendent Steel Production, Carnegie-Illinois Steel Corporation.



indicate excellent correlation between bath temperatures and tapping and pouring temperatures. We fail to see anything hazardous in either the instrument or the procedure of its application, and as a rule it has been accepted favorably by our melting crew.

C. A. ZAPFFE,\* Columbus, Ohio.—At Battelle Memorial Institute we have had occasion to measure temperatures of steel with an optical pyrometer by sighting through a tube that concurrently carried gas to the melt. Readings were taken with both a red and a green filter, to permit calculation of the emissivity of the steel. The composition, rate of flow and preheating conditions of the gas were all closely controlled. Two obvious sources of error in temperature measurement were noted:

1. There is a direct cooling of the surface of the melt, depending in degree upon the temperature and upon the rate of flow of the gas.
2. Oxidation of the steel by the incoming gas causes the emissivity of the surface to vary in an erratic, incalculable manner, which is further complicated by actual temperature differences resulting from the heats of oxidation.

R. B. SOSMAN.—Concerning the effect of hydrogen, it might be worth while to remark that the heat capacity of hydrogen and its thermal conductivity are both high. A good way to cool off an ingot of steel is to blow hydrogen through it. As to the surface in air, the dark parts would be the clean steel and the light would be the oxide or slag. That perhaps should have been mentioned in connection with the use of the optical pyrometer on tapping and pouring streams. It is not always recognized that the dark part of the stream is the clean steel and is the part that it is best to take the reading on. The light parts may be oxide or they may be just V-shaped grooves which are radiating as a full radiator or black body. The natural tendency of a man reading an optical is to sight on the light and neglect the dark.

T. S. WASHBURN.—Another difficulty of reading the pouring temperature with an optical pyrometer is to match the filament with the dark section of the stream, as Dr. Sosman has pointed out, and at the same time correct for the darkening effect of fumes between the instrument and the stream. When pouring into tar-dipped molds, or those coated with material that fumes during pouring, it is impossible at times to obtain a satisfactory temperature reading because of this condition.

W. O. PHILBROOK.—Has anyone any definite information for those of us who still have to use opticals as to how the emissivity varies with steels? Would a 3100 series steel with the same optical reading be anywhere near the corresponding temperature of a plain carbon steel?

M. F. YAROTSKY.—In our practice the emissivity factor is the same for both grades of steel. However, chromium, even in the range of the 3100 series, may contribute to occasional erratic readings, owing to a film of chromic oxide.

R. B. SOSMAN.—Concerning the emissivity, it is known that pure iron and cast iron high in carbon are, surprisingly enough, nearly alike, being both about 0.4, perhaps a little above that; but it is also known that small percentages of certain additions, such as manganese and chromium, do increase the brightness decidedly. I do not know of any measurement that shows any lower emissivity than the 0.4 of pure iron. In the case of additions that are known to increase the emissivity—that is, the brightness—readings taken on the liquid surface and corrected by the standard emissivity of 0.4 would give temperatures that are too high.

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\* Battelle Memorial Institute.



B. M. LARSEN.—In the use of the photoelectric cell for temperature measurements, we know the shape of the calibration curve, that is, the temperature-output curve, for a black-body condition, so that we can use that as an arbitrary scale, assuming that we have similar conditions in the bath.

### PLANT METHODS

Dr. C. H. Herty, Jr., of the Research and Development Department, Bethlehem Steel Co., Bethlehem, Pa., took the chair.

### METHODS OF STUDYING SLAGS

C. H. HERTY, JR.—The reason we study slags, of course, is to find what the effect of the slag is on the metal. We are not so much interested in the slag itself, but in the slag as a good or bad influence on the metal, and slags have been used as a criterion of good or bad metal ever since steelmaking began.

The general method of studying slags can be divided into the following groups, and if anybody can add anything to these groups, we will appreciate it.

First of all, there is the visual method, whereby the expert melter, or the not so expert metallurgist, looks in the furnace and decides what the slag needs. Other visual methods are involved in the taking of a slag sample, pouring on the floor or cooling under various conditions, and from the color of the slag and the texture of the slag, judging certain things about its composition. In this class comes the standardized color test which the old melters used, and also the more recent pancake test, described from time to time both in this country and abroad, in which the slag cake is poured into a special mold, the surface color and texture noted and that color and texture correlated with such things as the lime-silica ratio, the FeO content,  $P_2O_5$ , and other things more or less important.

Another method is the simple one of analyzing the slag. Some plants have become remarkably adept at rapid methods of analysis for slags. I know plants that will give an FeO determination to the melter in something like 8 or 10 min. after the sample was taken, and do it accurately and regularly. Lime and silica take considerably longer, sometimes 20 to 25 min., and very often that is a little bit too long for the average man, because in a good sharp working furnace  $\frac{1}{2}$  hr. can make a great deal of difference in the condition of the bath.

Another method of studying slags might be put under the general term "flow." We have used what we call a viscosimeter, which actually measures a combination of viscosity and distance above the melting point.

There are methods of determining flow other than this particular instrument. The old-time acid-open-hearth melter took out a sample of slag on the rod and watched it drip off, and that gave him a measurement corresponding to the viscosity test of today.

Another method is the petrographic, in which slag samples are examined under the microscope. Certain conclusions are drawn as to what is in the slag in the solid state, and from those are deduced the condition of the liquid state. One of the speakers this morning said that often that test is not satisfactory, but it does give some good correlations of what is dissolved in the slag and what is not.

Other properties, conductivity, magnetic properties, etc., are being studied and used for determining the conditions of slags, and, finally, a method mentioned this morning of using slag-metal reactions. That is a sort of backward way of doing a thing on the floor because it has to be post mortem. On the other hand, it is a nice way of doing it in the laboratory, particularly because the real thing we are interested in is the slag-metal reaction; so after all, if we could evolve a distinct method of studying slag reactions, we would be striking at the heart of the problem, and I

believe that some of our universities are now equipped to make a really good study of that method.

Under this session we have six or seven different topics. First of all is Laboratory Methods for Slag Viscosity. The general method of studying slags in the laboratory has particularly revolved on slag viscosity, and slag viscosity, as we know, is an important item in the open hearth or the blast furnace. R. S. McCaffery and A. L. Feild both used the standard concentric cylinder method of studying slag viscosity, and I might say that Mr. Feild, with P. H. Royster, really originated, as far as ferrous metallurgy is concerned, the work on viscosity on blast-furnace slags.

On methods for sampling slag in the open hearth, Mr. Yarotsky will speak.

### Sampling Slag in the Open Hearth

M. F. YAROTSKY.—Sampling of slag by means of visual examination of slag pancake has proved, in our experience, to be a practical and efficient method of slag control. It enables the furnace operator to judge the oxidation as well as the relative basicity of the slag within the short interval of time necessary for the sample to cool off.

Furthermore, petrographic studies of open-hearth slags at our plant reveal that visual examination of slag pancakes may be correlated with the petrographic structure of the slag and to a degree with its composition. There is a correlation between the visual character of slag and the amount and types of minerals in it, as determined by petrographic analysis, which gives particular significance to this method of slag control.

The question may be raised on the relative efficiencies of this method of arriving at the desired slag composition as well as its reliability, in comparison to a laboratory determination. At this time we consider the method sufficiently established to dispense with analytical determination for iron in the slag on most grades of steel. In recent investigations on several grades of steel, we found that visual examination of slag pancakes for iron content has checked simultaneous analytical determination within 1 per cent on approximately 75 per cent of the tests, and that 90 per cent of the tests came within 2 per cent of analytical examination. In practice, 80 to 90 per cent of all heats are within the 4 per cent specified range of slag oxidation.

W. O. PHILBROOK.—We have just begun to train our melters in the practice just discussed. Our slag control now is based more on a total iron determination. We have found from experience that depending upon the method of sampling, the slag  $\text{FeO}$  could be oxidized to  $\text{Fe}_2\text{O}_3$  by contact with the air, and also samples from different levels in the slag could be somewhat different, and as a practical tool we think that we can get a better indication of the oxidizing power of the slag by running the analysis for total iron, the sample being cooled in any reasonable method.

### Viscosity of Open-hearth Slags

C. H. HERTY, JR.—I might say in connection with the next subject, viscosity of open-hearth slags, that a viscosimeter gives a good deal of information about composition until fluorspar is added to the heat, and after that the effect of the spar overbalances the effect of other constituents in the slag. So after the fluorspar addition, I am sure that the visual examination is extremely important.

One question I would like to ask Mr. Yarotsky: Does fluorspar in large amounts have any particular effect on the estimation of lime-silica ratios and  $\text{FeO}$ ?

M. F. YAROTSKY.—The addition of fluorspar in large amounts does not interfere with the estimates of the lime-silica ratio, although it obliterates visible characteristics on the top surface of a pancake that indicate the iron content of the slag. Practice at South Works is to keep the use of fluorspar at a minimum, which does not interfere with the efficiency of this method.

C. H. HERTY, JR.—Of course the value of any method lies in the method of its application. We are not supposed to go into that today; nevertheless, it would be worth knowing if you could apply it. Mr. Reagan, at the Edgewater Steel Co., has made use of various methods of slag control and methods of determining the composition of the slag. We will not ask him to say anything about the application, but we will ask him to give a little idea of what is used in his plant and whether he thinks it is satisfactory.

W. J. REAGAN,\* Pittsburgh, Pa.—We have used the viscosimeter as a means of determining slag fluidities for a number of years. We like it very much. It converts slag fluidity into a numerical factor such as inches, which gives much more accurate figures for relative fluidities than terms such as "heavy," "thin" or "creamy."

We have used the pancake method of slag sampling, with results similar to some already described. In reading these samples the results must be taken with a grain of salt. The only thing we have been able to find is that it gives some idea of the lime-silica ratio. Most of our steels are the higher carbons, 0.40 to 0.80 per cent, and the lime-silica values do not vary a great deal.

Along this line an interesting thing happened some time ago at a class I have at Carnegie School of Technology. We were discussing pancake samples and some of the boys were sure that they could read any sample quite accurately. It was suggested that samples be brought into class from a number of shops and the boys be allowed to read the samples. We had about 15 or 20 samples from different shops with fairly large ranges of FeO and the lime-silica ratios. When the boys tried to read the samples from plants other than their own they were absolutely at sea, and could tell nothing about them at all, except that for a few they could give a rough idea of the lime-silica ratio.

It has been our experience, and this fact seems to be verified by others, that unless you have the background of the heat, the carbon drop, ore and lime additions, etc., to go along with the samples, the results are not of much value. In our particular case I believe other factors such as fluidity, residual phosphorus and manganese, and an occasional iron oxide, give a much better picture of the condition of our heat and of what is going on at the time the samples were taken.

C. H. HERTY, JR.—It is fortunate that whenever we take out a sample we always have the history. That is what makes it so easy for many people to read fracture carbons; they know what the last one was.

We find the viscosity tests about which Mr. Reagan has just spoken particularly good rather early in the heat, where they give an idea as to whether the heat is going to be deficient in lime or overlimed. In the present stage of the game, I believe that pig iron today is much better than we used to get, from the standpoint of uniformity, nevertheless we do get a swing in silicon content of the pig iron and even though we may try to compensate for that in the charge, we still make a mistake occasionally, and to know early in the heat whether there is any deficiency is an advantage.

#### Petrographic Examination of Slag

G. SOLER,† Canton, Ohio.—Fig. 1 shows a chart of a 100-ton open-hearth heat from melt to tap. I chose this heat because it has a high amount of silicon and manganese going into the latter part of the heat. We obtained slag pancakes, analyses of steel and slag, and made petrographic thin-section examinations at 20 diameters and at 300 diameters. We also examined powder sections to determine the mineralogical phases present.

\* Edgewater Steel Co.

† Research Manager, Steel and Tube Division, Timken Roller Bearing Co.

The heat melted at 0.87 per cent carbon, and was given two shots of ore, 4000 lb. after the melt and 2000 lb. later. After the ore had worked out, a test was taken, the heat reboiled with 1200 lb. of spiegel, spar added, more tests taken, and then the heat blocked with 15 per cent silicon. Manganese was added in three different additions;

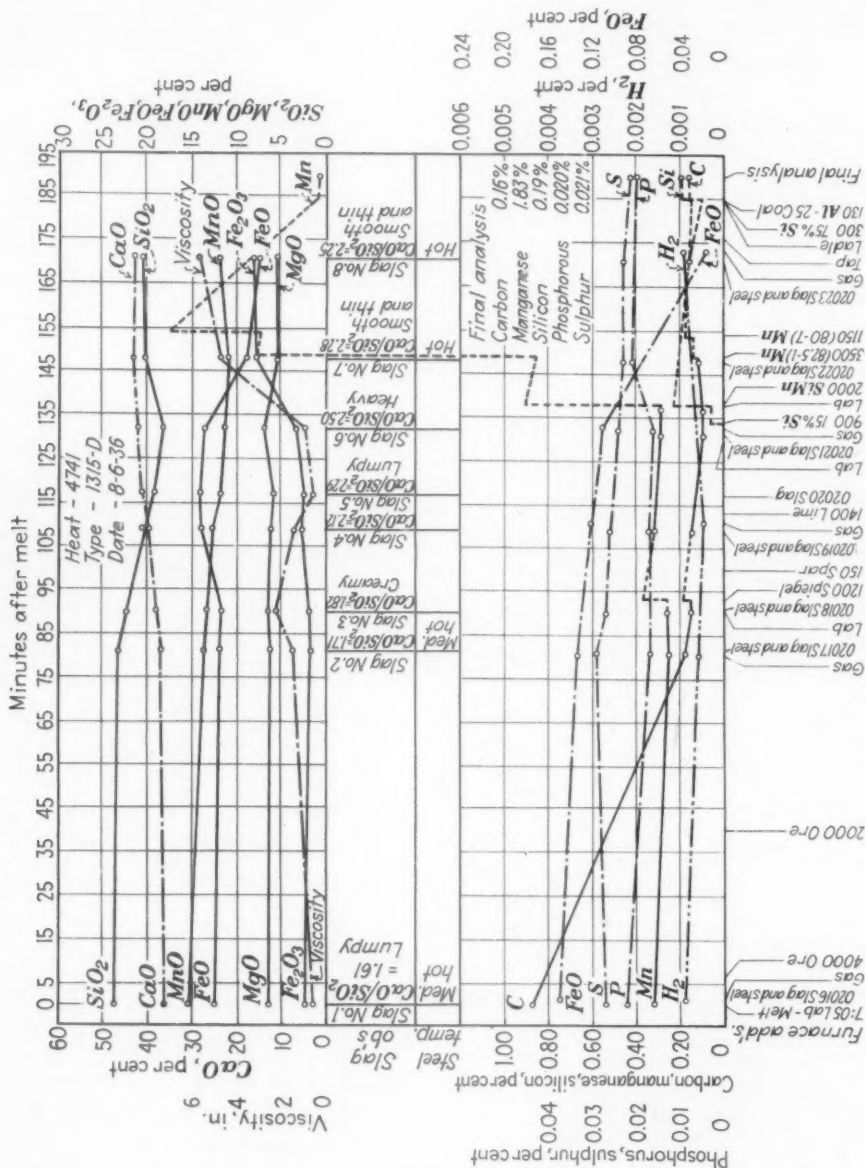


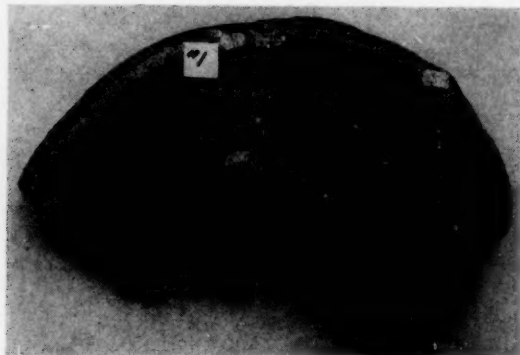
Fig. 1.—Chart of 100-ton open-hearth heat from melt to tap.

the first as silicon manganese, the others as 80 per cent ferromanganese. Eight slag samples were taken.\*

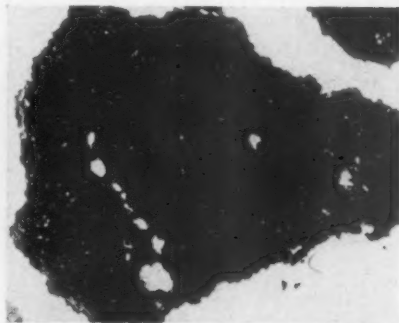
The slag pancakes (Fig. 2) are shown for those who use slag pancakes. We do not use them as a method of control, primarily because we use a cold pig charge and we know fairly well the silicon content in the bath, the amount of silica formed, and the

\* Petrographic work and photographs by R. K. Lee, Research Department, Timken Roller Bearing Co.





Surface.  $\frac{1}{2}$  actual size. Surface appeared dull dark gray.



Photomicrograph of thin section. Original  $\times 20$ . Reduced  $\frac{1}{2}$  in reproduction.

Small white areas and lines are  $\text{CaO} \cdot \text{RO} \cdot \text{SiO}_2$  and  $2\text{CaO} \cdot \text{SiO}_2$ .

Large white areas are holes. This sample was exceedingly fine grained.



Fracture.  $\times 2$ . Extremely porous and friable. Holes dull black. Large amount of shot steel.



Photomicrograph of thin section. Original  $\times 300$ . Reduced  $\frac{1}{2}$  in reproduction.

The large white areas are  $2\text{CaO} \cdot \text{SiO}_2$ . Smaller white areas within dark grains are  $\text{CaO} \cdot \text{RO} \cdot \text{SiO}_2$ .

Round dark spots are the yellowish brown cubic phase, probably a spinel type compound.

FIG. 2.—SAMPLE TAKEN AT MELT. POURED SLIGHTLY LUMPY. VISCOSITY  $\frac{5}{8}$  INCH. SLAG No. 1.

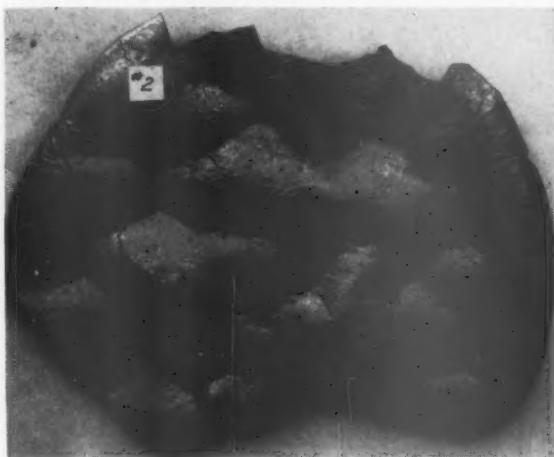
Chemical analysis:  $\text{CaO}$ , 35.89;  $\text{SiO}_2$ , 23.76;  $\text{FeO}$ , 12.38;  $\text{Fe}_2\text{O}_3$ , 2.24;  $\text{MnO}$ , 15.42;  $\text{MgO}$ , 6.44;  $\text{CaO} \cdot \text{SiO}_2$ , 1.615.

limestone charged, and we can more or less predict what lime-silica ratio we will have at the end of the heat.

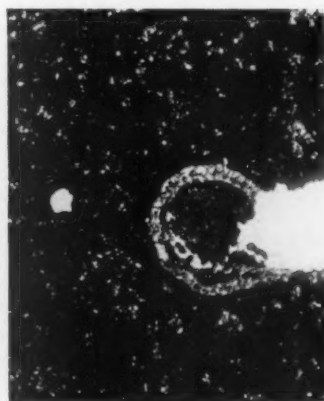
The petrographic microscope, we can say, is a tool for determining the course of reactions and the undissolved phases that might be present in the slag. Some people may take exception to the fact that studies of chilled slag samples are used to determine the nature of the liquid slag, and question the existence of any heterogeneity. However, we find undissolved phases in these slags when we look at them through the petrographic microscope. Quenched slag samples do not show a great deal of difference in phases found, compared to slowly cooled samples.

In regard to physical groupings in liquid slag, we feel it is made up of positively and negatively charged ions. The  $\text{SiO}_4^{4-}$  ions tend to hold the calcium, manganese, iron, and magnesium ions. They may not be held completely in place, but we feel that at any given time, though the ions are continually changing position, certain ones such as  $\text{Ca}^{++}$  will be more closely linked to  $\text{SiO}_4^{4-}$ . Such preferential affinities will account for the effect of lime-silica ratios on manganese, phosphorus and iron oxide.





Surface.  $\frac{1}{2}$  actual size. Surface dull steel gray.



Photomicrograph of thin section. Original  $\times 20$ . Reduced  $\frac{1}{2}$  in reproduction.

White rim around grain and white spots outside grain are  $2\text{CaO} \cdot \text{SiO}_2$ . White spots within grain are  $\text{CaO} \cdot \text{RO} \cdot \text{SiO}_2$ .

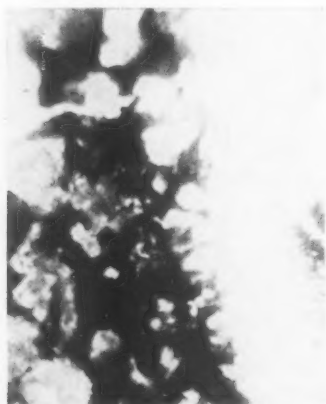


Fracture.  $\times 2$ . Porous and showing nonuniform brown spots in the dull dark gray fracture.

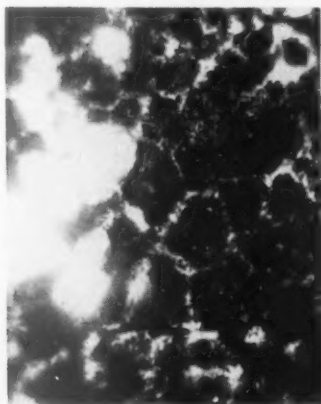


Photomicrograph of thin section. Original  $\times 300$ . Reduced  $\frac{1}{2}$  in reproduction.

Dark cleaved area large grain of  $\text{MgO}$  showing very small reaction rim. White areas  $2\text{CaO} \cdot \text{SiO}_2$ .



Photomicrograph of thin section. Original  $\times 300$ . Reduced  $\frac{1}{2}$  in reproduction. White area  $2\text{CaO} \cdot \text{SiO}_2$  reaction rim seen above. Gray areas  $\text{CaO} \cdot \text{RO} \cdot \text{SiO}_2$  within grain.

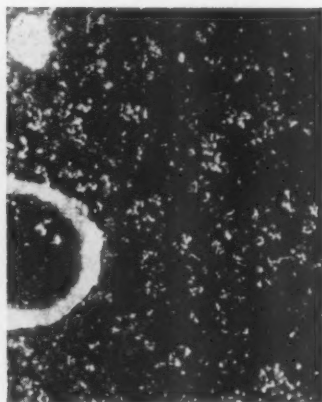


Photomicrograph of thin section. Original  $\times 300$ . Reduced  $\frac{1}{2}$  in reproduction. Typical view of thin section. White areas are  $2\text{CaO} \cdot \text{SiO}_2$ ; dark dendrites brownish cubic phase.

FIG. 3.—SAMPLE TAKEN 80 MINUTES AFTER MELT AFTER 6000 POUNDS ORE HAD WORKED OUT OF SLAG. POURED SMOOTH. VISCOSITY  $1\frac{1}{2}$  INCH. SLAG No. 2.  
Chemical analysis:  $\text{CaO}$ , 37.30;  $\text{SiO}_2$ , 23.30;  $\text{FeO}$ , 12.10;  $\text{Fe}_2\text{O}_3$ , 1.75;  $\text{MnO}$ , 13.82;  $\text{MgO}$ , 6.25;  $\text{CaO} \cdot \text{SiO}_2$ , 1.716.



Surface.  $\frac{1}{2}$  actual size. Rough, light steel gray, semi-dull.

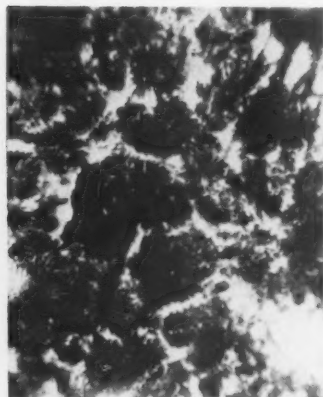


Photomicrograph of thin section. Original  $\times 20$ . Reduced  $\frac{1}{2}$  in reproduction.

White  $2\text{CaO.SiO}_2$  reaction rim around partly dissolved  $\text{CaO}$  lump.

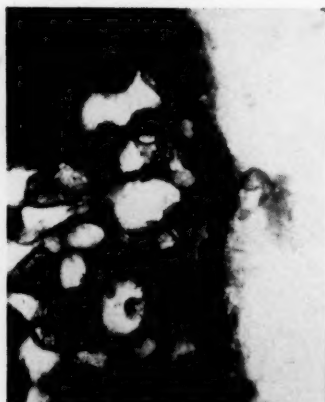


Fracture.  $\times 2$ . Somewhat porous. Shows heterogeneity with brown undissolved particles in a black matrix.

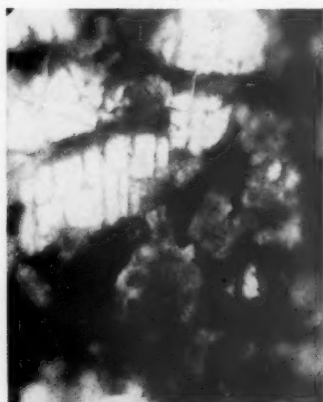


Photomicrograph of thin section. Original  $\times 300$ . Reduced  $\frac{1}{2}$  in reproduction.

Typical appearance of this slag. White areas,  $2\text{CaO.SiO}_2$ ; dark dendrite, yellowish brown cubic phase.



Photomicrograph of thin section. Original  $\times 300$ . Reduced  $\frac{1}{2}$  in reproduction. Border between reaction rim and  $\text{CaO}$  lump. White area on outside and those inside are  $2\text{CaO.SiO}_2$ . Gray area in white is yellow cubic phase.



Photomicrograph of thin section. Original  $\times 300$ . Reduced  $\frac{1}{2}$  in reproduction.

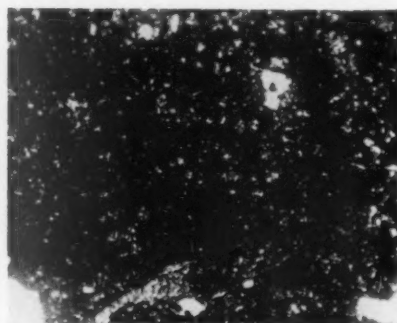
Interior of lime lumps. Cleaved white areas are undissolved  $\text{CaO}$ . Mussy gray areas are  $2\text{CaO.SiO}_2$ .

FIG. 4.—SAMPLE TAKEN 90 MINUTES AFTER MELT, 10 MINUTES AFTER SLAG NO. 2 AND 3 MINUTES BEFORE 1200 POUNDS SPIEGEL ADDED TO BATH. SAMPLE POURED CREAMY. VISCOSITY  $2\frac{1}{4}$  INCHES. SLAG NO. 3.

Chemical analysis:  $\text{CaO}$ , 38.24;  $\text{SiO}_2$ , 22.52;  $\text{FeO}$ , 11.95;  $\text{Fe}_2\text{O}_3$ , 1.92;  $\text{MnO}$ , 13.31;  $\text{MgO}$ , 6.49;  $\text{CaO.SiO}_2$ , 1.821.



Surface.  $\frac{1}{2}$  actual size. Darker steel gray, smooth and slightly glossy.

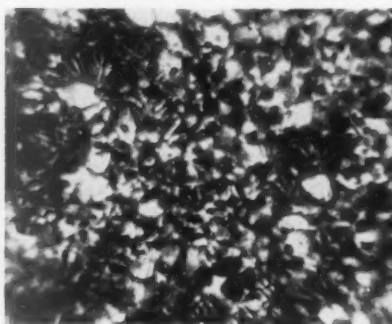


Photomicrograph of thin section. Original  $\times 20$ . Reduced  $\frac{1}{2}$  in reproduction.

Small white areas are  $2\text{CaO} \cdot \text{SiO}_2$ . Large white areas are holes. Large cluster of white crystals near edge are  $2\text{CaO} \cdot \text{SiO}_2$ .



Fracture.  $\times 2$ . More dense. Holes dull black. Fine grained. Few brown undissolved particles.



Photomicrograph of thin section. Original  $\times 300$ . Reduced  $\frac{1}{2}$  in reproduction.

Typical high magnification appearance of this slag in thin section. White areas are  $2\text{CaO} \cdot \text{SiO}_2$ . Dark areas are the yellow-brown cubic phase, probably of spinel character.

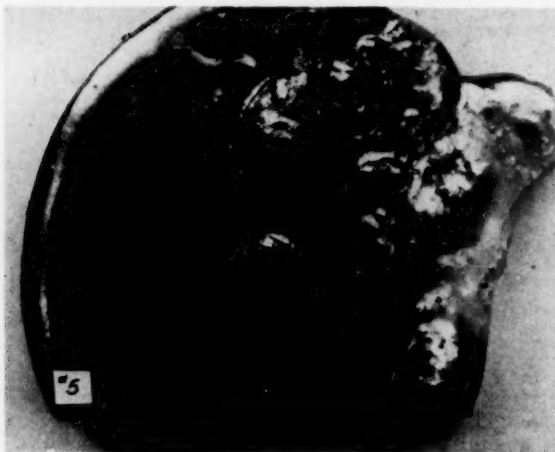
FIG. 5.—SAMPLE TAKEN 19 MINUTES AFTER SLAG NO. 3 AND 9 MINUTES AFTER 150 POUNDS SPAR ADDED TO SLAG. SLAG POURED SMOOTH. VISCOSITY  $1\frac{3}{8}$  INCH. SLAG NO. 4.

Chemical analysis:  $\text{CaO}$ , 39.84;  $\text{SiO}_2$ , 20.18;  $\text{FeO}$ , 13.97;  $\text{Fe}_2\text{O}_3$ , 2.88;  $\text{MnO}$ , 12.80;  $\text{MgO}$ , 6.18;  $\text{CaO} \cdot \text{SiO}_2$ , 2.12.

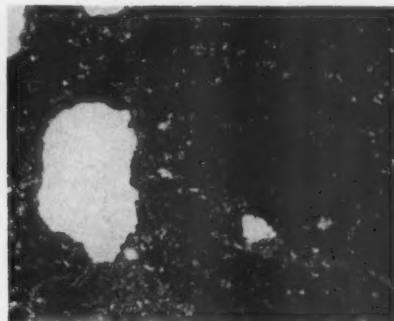
There are two main phases,  $2\text{CaO} \cdot \text{SiO}_2$  and  $\text{CaO} \cdot \text{RO} \cdot \text{SiO}_2$ . The RO can be manganese oxide, iron oxide ( $\text{FeO}$ ), magnesium oxide, or calcium oxide. The samples taken at 300 magnifications show a dark yellow-brown cubic phase, which has been quite liquid, indicating by the manner the crystals separated out that it crystallized last because of its lower melting point.

In the upper photograph of Fig. 3 can be seen a dicalcium-silicate rim. It was originally around a lime particle. These rims persist throughout the heat, indicating that the slag is not a completely homogeneous solution until the last stages of the heat. In thin section is shown a particle of periclase ( $\text{MgO}$ ), which dissolves very slowly in the slag.

The dicalcium silicate rim (Fig. 4) continues in the third slag sample. In the lower photomicrograph are shown some cleaved sections of lime lump. The dicalcium



Surface.  $\frac{1}{2}$  actual size. Dark metallic luster.

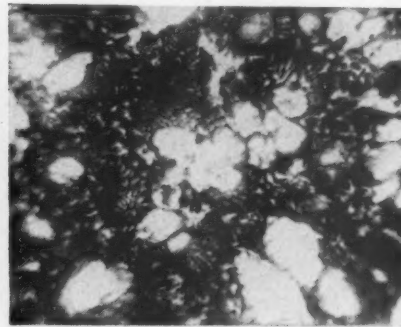


Photomicrograph of thin section. Original  $\times 20$ . Reduced  $\frac{1}{2}$  in reproduction.

Small white dots are  $2\text{CaO} \cdot \text{SiO}_2$ . Large white areas are holes.



Fracture.  $\times 2$ . Large holes lined with tiny black crystals. Numerous undissolved particles.



Photomicrograph of thin section. Original  $\times 300$ . Reduced  $\frac{1}{2}$  in reproduction.

Typical appearance of this slag in thin section. White areas are  $2\text{CaO} \cdot \text{SiO}_2$ . Dark round areas and dendrites are the yellow-brown cubic phase.

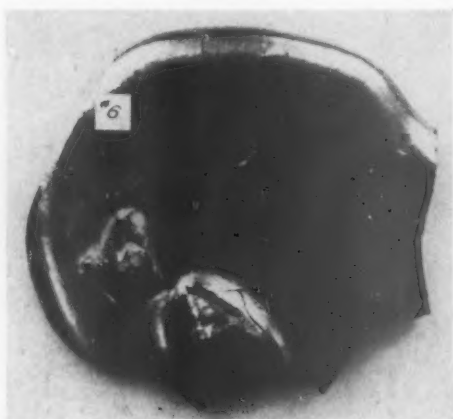
FIG. 6.—SAMPLE TAKEN 8 MINUTES AFTER SLAG NO. 4 AND 4 MINUTES AFTER 1400 POUNDS LIME ADDITION TO SLAG. POURED LUMPY. VISCOSITY  $\frac{5}{8}$  INCH. SLAG No. 5.

Chemical analysis:  $\text{CaO}$ , 41.44;  $\text{SiO}_2$ , 19.36;  $\text{FeO}$ , 14.11;  $\text{Fe}_2\text{O}_3$ , 2.56;  $\text{MnO}$ , 12.03;  $\text{MgO}$ , 5.98;  $\text{CaO} \cdot \text{SiO}_2$ , 2.294.

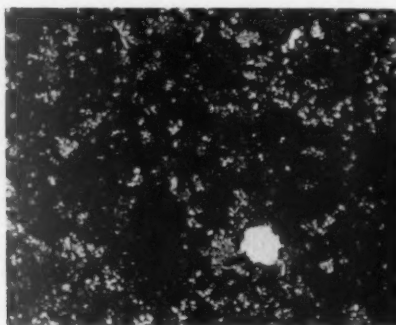
silicate is increasing and the  $\text{CaO} \cdot \text{RO} \cdot \text{SiO}_2$  phase has more or less disappeared at 1.82 lime-silica ratio. This seems rather queer, but we find this in all our samples. Apparently the  $\text{CaO} \cdot \text{RO} \cdot \text{SiO}_2$  phase forms a solid solution with the dicalcium silicate at about 1.75 up to 2.0 lime-silica ratio.

In Fig. 5, there can still be seen a portion of the dicalcium silicate, in the lower part of the upper right-hand petrographic section. In Fig. 6, dicalcium silicate can be seen still existing in undissolved form.

At a 2 to 1 ratio or slightly higher the slags ordinarily make a change in the state of the iron oxide. The  $\text{Fe}_2\text{O}_3$  increases, and if a slag sample is powdered and observed visually, it appears reddish brown. This change is indicated under the microscope by a change in the yellow-brown cubic phase to a more reddish color.



Surface,  $\frac{1}{2}$  actual size. Glossy, metallic luster. Dark steel gray.

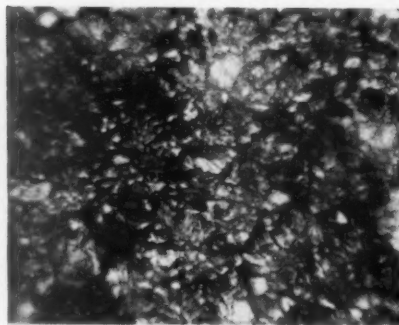


Photomicrograph of thin section. Original  $\times 20$ . Reduced  $\frac{1}{2}$  in reproduction.

White clusters are  $2\text{CaO} \cdot \text{SiO}_2$ . Large white area is a hole.



Fracture,  $\times 2$ . Dense and fine grained with faint brownish black color. Fewer undissolved particles.



Photomicrograph of thin section. Original  $\times 300$ . Reduced  $\frac{1}{2}$  in reproduction.

General appearance of this slag in thin section. White areas  $2\text{CaO} \cdot \text{SiO}_2$ . Dark and gray areas are the yellow-brown cubic phase.

FIG. 7.—SAMPLE TAKEN 15 MINUTES AFTER SLAG NO. 5 AND BEFORE 900 POUNDS 15 PER CENT SILICON ADDITION. POURED HEAVY. VISCOSITY 1 INCH. SLAG NO. 6.

Chemical analysis:  $\text{CaO}$ , 42.80;  $\text{SiO}_2$ , 18.32;  $\text{FeO}$ , 13.68;  $\text{Fe}_2\text{O}_3$ , 3.36;  $\text{MnO}$ , 11.46;  $\text{MgO}$ , 6.87;  $\text{CaO} \cdot \text{SiO}_2$ , 2.505.

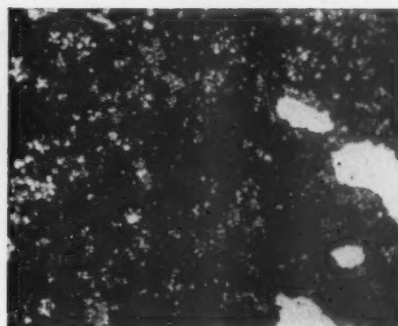
In slag No. 6 the dicalcium silicate is pretty well dissolved and the small white particles are the normal crystals of dicalcium silicate (Fig. 7). The slag is becoming more homogeneous. The dark gray areas in the lower picture have crystallized as dendrites around the dicalcium silicate crystals, indicating a more fluid phase. Fig. 8 shows about the same type of slag. The dendrites are shown a little better in the lower picture. Fig. 9 shows the tapping slag.

One point that can be gathered from this type of data is viscosity relations. Dicalcium silicate has a very high melting point and as it increases throughout the heat in the transformation from the olivine phase, because of building up of lime content, the slag becomes more viscous, as was shown in Fig. 1. Then as the  $\text{FeO}$  to  $\text{Fe}_2\text{O}_3$  ratio changes and  $\text{Fe}_2\text{O}_3$  builds up after passing the 2 to 1 lime-silica ratio, the slag ordinarily become more fluid, and that may be affected in turn by the  $\text{MnO}$ - $\text{FeO}$  solid solution



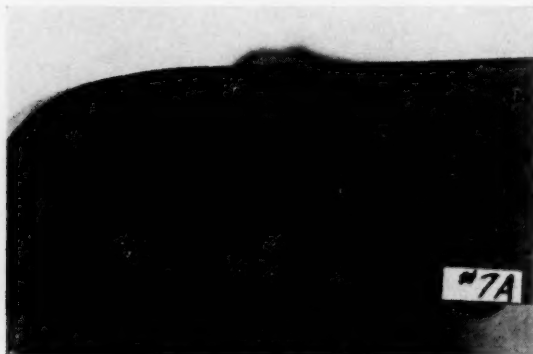


Surface,  $\frac{1}{2}$  actual size. Glossy submetallic luster and dark gray color. Smooth.

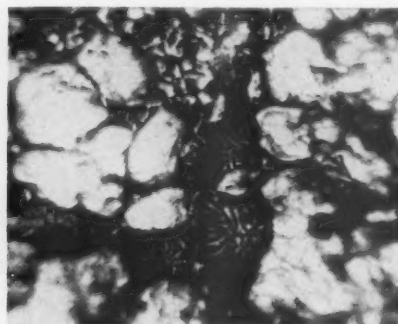


Photomicrograph of thin section. Original  $\times 20$ . Reduced  $\frac{1}{2}$  in reproduction.

Small white clusters are  $2\text{CaO.SiO}_2$ . Large white areas are holes.



Fracture,  $\times 2$ . Dense, homogeneous, fine grained.



Photomicrograph of thin section. Original  $\times 300$ . Reduced  $\frac{1}{2}$  in reproduction.

Typical appearance of this slag in thin section. White areas are  $2\text{CaO.SiO}_2$ . Dark areas and dendrites are the yellow-brown cubic phase.

FIG. 8.—SAMPLE TAKEN 16 MINUTES AFTER SLAG NO. 6 AND 10 MINUTES AFTER 2000 POUNDS SILICON-MANGANESE ADDITION. POURED SMOOTH AND THIN. VISCOSITY  $4\frac{3}{4}$  INCHES. SLAG NO. 7.

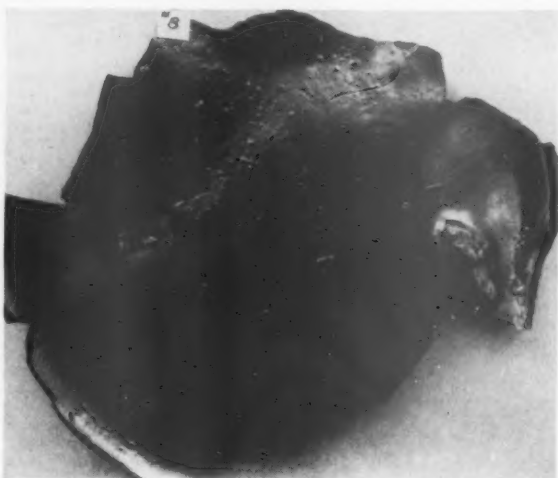
Chemical analysis:  $\text{CaO}$ , 43.40;  $\text{SiO}_2$ , 20.42;  $\text{FeO}$ , 8.93;  $\text{Fe}_2\text{O}_3$ , 8.00;  $\text{MnO}$ , 11.33;  $\text{MgO}$ , 5.34;  $\text{CaO.SiO}_2$ , 2.278.

phase, described by McCaughey at the last open-hearth meeting,<sup>1</sup> which may impart fluidity below the 2 to 1 lime-silica ratio, and also above this ratio. Its composition varies, therefore its fluidity may vary. The subject was also covered by Earl Smith in the 1935 Howe Memorial Lecture.<sup>2</sup>

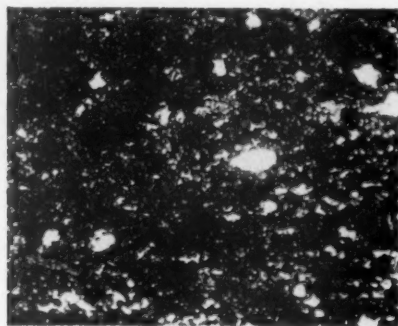
Three types of  $\text{CaO-Fe}_2\text{O}_3$  linking may be seen in petrographic samples. One is the yellow-brown cubic phase with high-carbon steels, a reddish brown cubic phase in low-carbon steels and reddish black calcium ferrite with ingot-iron very highly oxidized slags.

<sup>1</sup> W. J. McCaughey: 21st Open Hearth Proceedings (1938) 167. A.I.M.E.

<sup>2</sup> *Trans. A.I.M.E.* (1935) 116, 13.



Surface.  $\frac{1}{2}$  actual size. Bluish submetallic luster. Smooth.

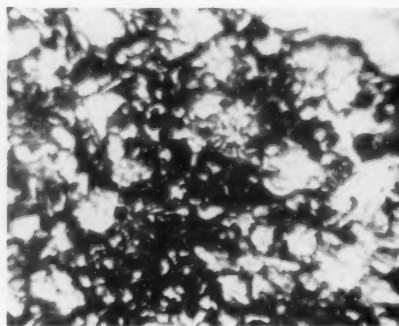


Photomicrograph of thin section. Original  $\times 20$ . Reduced  $\frac{1}{2}$  in reproduction.

Small white clusters are  $2\text{CaO} \cdot \text{SiO}_2$ . Large white areas are holes.



Fracture.  $\times 2$ . Very dense and fine grained. Black and dull fracture.



Photomicrograph of thin section. Original  $\times 300$ . Reduced  $\frac{1}{2}$  in reproduction.

Typical appearance of this slag in thin section. White areas are  $2\text{CaO} \cdot \text{SiO}_2$ . Dark areas are the yellow-brown cubic phase.

FIG 9.—SAMPLE TAKEN 23 MINUTES AFTER SLAG NO. 7 AND 5 MINUTES BEFORE TAP.

POURED SMOOTH AND THIN. VISCOSITY  $5\frac{3}{4}$  INCH. SLAG NO. 8.

Chemical analysis:  $\text{CaO}$ , 43.24;  $\text{SiO}_2$ , 20.60;  $\text{FeO}$ , 7.92;  $\text{Fe}_2\text{O}_3$ , 8.00;  $\text{MnO}$ , 11.97;  $\text{MgO}$ , 5.29;  $\text{CaO} \cdot \text{SiO}_2$ , 2.250.

MEMBER.—Do you make any routine use of it?

G. SOLER.—No, we do not. In 1932, before slag pancakes came into vogue we used the petrographic microscope to control the lime-silica ratio on a series of experimental heats. We took samples on the floor, crushed them, and made our examination in about 10 min. Petrographic thin sections require an hour for preparation of the sample and examination. Thin sections are necessary for the study of slag maturity and undissolved phases. The melter with proper judgment can determine the shape or maturity of the slag (undissolved phases) and with a known charge can reliably predict lime-silica ratios.

STATISTICAL METHODS APPLIED TO STUDY AND CONTROL OF  
CHEMICAL REACTIONS IN BATH

## Rapid Method of Correlation Applicable to Study of Steelmaking Reactions

BY KARL FETTERS\*

At the Massachusetts Institute of Technology a program of investigation of the reactions associated with steelmaking is being carried out under the direction of Dr. John Chipman. Laboratory investigations are being supplemented by studies of open-hearth data representing various steel plants and practices. The open-hearth tests have been taken according to modern practices of slag and metal sampling as described by McCutcheon and Rautio. In the preparation for study of the plant figures two aims have been held constantly in mind. The first has been to obtain an adequate criterion of the degree of relationship, or correlation, between any two variables under consideration. The second has been to facilitate the analysis of the data with a minimum of time and effort. The analysis rapidly assumes enormous proportions when more than a few correlations are desired, particularly in the case of extensive subclassification of large amounts of data.

The application of statistical methods to the study of metallurgical problems has been pointed out by Chancellor,<sup>1</sup> Hand,<sup>2</sup> Hoar,<sup>3</sup> Norris,<sup>4</sup> Daeves,<sup>5</sup> Hayes and Passano,<sup>6</sup> and others. Their applications and illustrations in general have been related to the control of quality and its relation to the manufacturing variables.

As a means of facilitating the handling of data in such studies, Reagan<sup>7</sup> and McCaffery and Stephenson<sup>8</sup> have made use of tabulating cards of the type used in accounting methods for many years. The use of cards greatly increases the number of data that may be considered and makes possible extensive subclassifications that otherwise would be out of the question.

In order to illustrate the methods, certain interesting results of a preliminary study of the plant designated as E have been used. Complete results of the entire study will be available later.

Correlation methods have been quite generally applied in statistical analyses, particularly in the fields of biology and education, and are discussed in any general textbook on statistics. It suffices here to note that the correlation coefficient  $r$  varies from minus one through zero to plus one, the approaches to plus or minus one characterizing increasingly good relationship between the two variables. The significance of correlation coefficients may be determined by the methods of R. A. Fisher.<sup>9</sup>

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<sup>1</sup> W. C. Chancellor: Applications of Statistical Methods to the Solution of Metallurgical Problems in the Steel Plant. *Proc. Amer. Soc. Test. Mat.* (1933) **34**, 891.

<sup>2</sup> H. J. Hand: Utility of Statistical Methods in Steel Plants. *Trans. A.I.M.E.* (1938) **131**, 231.

<sup>3</sup> T. P. Hoar: Statistical Correlation and Metallurgical Problems. *Metallurgist* (June 26, 1936) 134.

<sup>4</sup> F. G. Norris: Significance of Slag Control. Unpublished.

<sup>5</sup> K. H. Daeves: Utilization of Statistics. *Testing* (March 1924).

<sup>6</sup> A. Hayes and R. F. Passano: Statistical Control. *Metal Progress* (Sept. 1931).

<sup>7</sup> W. J. Reagan: Slag Control for Basic Open-hearth High-carbon Steel. *Trans. A.I.M.E.* (1935) **116**, 107.

<sup>8</sup> McCaffery and Stephenson: A Statistical Analysis of Blast-furnace Data. *Trans. A.I.M.E.* (1931) **95**, 60. Iron and Steel Division.

<sup>9</sup> R. A. Fisher: Statistical Methods for Research Workers, Ed. 7. London. Oliver and Boyd.

Strictly speaking, these correlation methods are applicable only to the cases where the relation between the two variables is linear in nature. Slight to moderate departures from linearity do not detract markedly from the utility of these methods. Where the relation becomes decidedly curvilinear, a transformation of variable, such as to a reciprocal or logarithm, may often satisfactorily yield a linear relation. Failure to obtain a significant correlation may be due to one or more of the following: (1) lack of any real correlation; (2) an obscuring of the relation by other intercorrelations; (3) a very definite departure from linearity.

If a relation exists between two variables  $X$  and  $Y$ , it is usually desirable to represent that relation graphically by fitting a line to the scattered points. The equation of such a line, determined by least-squares methods, may be obtained simultaneously with the calculation of the correlation coefficient. We have used the so-called line of regression of  $Y$  on  $X$ , which corresponds to the average values of  $Y$ . Limits about

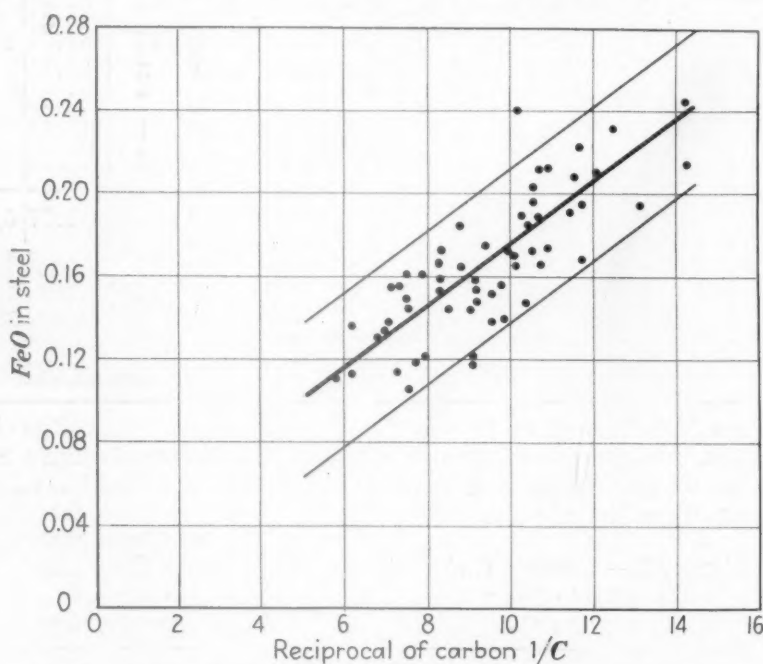


FIG. 1.—RELATION BETWEEN  $\text{FeO}$  IN THE STEEL AND RECIPROCAL OF THE CARBON. Data from 59 heats, plant E;  $r = 0.842$ . Limits shown are  $2\sigma$ .

this line of plus or minus twice the standard error of  $Y$  will include 95 per cent of the observed values in the case of normal distribution.

The tabulating cards in use are of the standard 80-column International Business Machine type and have been designed to include the following information: test identity; steel sample analyses for C, Mn, S, P, and  $\text{FeO}$ ; slag analyses for  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{MnO}$ ,  $\text{MgO}$ , S; and the calculated values of lime-silica ratio, ratio of ferrous oxide of slag to metal, total iron of slag calculated to  $\text{FeO}$ , the product of carbon and  $\text{FeO}$  in the steel, and three evaluations of the manganese constant. These cards are punched in an alphabetic duplicating printing punch which gives a visual record. After the cards have been properly arranged by being passed through the standard sorting machine, they are passed through a tabulating or listing machine, which lists and adds any desired combination of the figures. Here at the Institute there is available through the Division of Industrial Cooperation a listing machine, which, after suitable sorting of the cards, furnishes a record (Table 1). A few calcula-

TABLE 1.—*Sample Calculations of Tabulated Figures for Correlation of FeO<sub>steel</sub> with 1/C*

Results of First Pass through Listing Machine <sup>a</sup>						Results of Second Pass through Listing Machine			
(A) FeO in Steel	(B) Number of Heats	(C) Sum of FeO	(D) Sum of (FeO) <sup>2</sup>	(E) Sum of 1/C	(F) Sum of (FeO)(1/C)	(G) 1/C	(H) No. Heats	(I) Sum of 1/C	(J) Sum of (1/C) <sup>2</sup>
0.10-0.11	1	0.106	0.011130	7.69	0.80745	5-6	1	5.81	31.955
0.11-0.12	3	0.341	0.039215	19.33	2.22295	6-7	4	26.17	170.105
0.12-0.13	3	0.361	0.045125	24.96	3.12000	7-8	11	83.43	625.725
0.13-0.14	4	0.538	0.072630	27.09	3.65715	8-9	10	84.97	722.245
0.14-0.15	9	1.304	0.189080	78.89	11.43905	9-10	8	74.54	708.130
0.15-0.16	6	0.935	0.144925	52.23	8.09565	10-11	15	157.36	1,652.280
0.16-0.17	10	1.646	0.271590	91.43	15.08595	11-12	5	58.40	671.600
0.17-0.18	5	0.869	0.152075	49.28	8.62400	12-13	2	24.55	306.875
0.18-0.19	3	0.558	0.103230	30.05	5.55925	13-14	1	13.16	177.660
0.19-0.20	5	0.971	0.189345	57.25	11.16375	14-15	2	28.58	414.410
0.20-0.21	3	0.618	0.126690	34.21	7.01305				
0.21-0.22	3	0.637	0.136955	35.91	7.72065			556.97	5,480.985
0.22-0.23	1	0.223	0.050175	11.76	2.64600				
0.23-0.24	1	0.234	0.054990	12.50	2.93750				
0.24-0.25	2	0.484	0.118580	24.39	5.97555				
Totals.....	59	9.825	1.705735	556.97	96.06795				

<sup>a</sup> Columns A, B, C, E, G, H, I recorded by listing machine. Quantities of column D = midpoint of class interval shown in A times C; quantities of column F = midpoint of class interval shown in A times E; quantities of column J = midpoint of class interval shown in G times I.

TABLE 2.—*Sample Calculation of Correlation Coefficient*

Subject: Preliminary Study Plant E      Date: January 19, 1939

Variable X, 1/C

Variable Y, FeO in Steel

BASIC DATA			
	1/C		FeO
$\Sigma X$	556.97	$\Sigma Y$	9.825
$\Sigma X^2$	5480.985	$\Sigma Y^2$	1.705735
$N$	59	$\Sigma XY$	96.06795

$$\bar{X} = \frac{\Sigma X}{N} = 9.4402$$

$$\bar{Y} = \frac{\Sigma Y}{N} = 0.16653$$

$$\sigma_X = \sqrt{\frac{\Sigma(X)^2}{N} - \frac{(\Sigma X)^2}{(N)^2}}$$

$$= 1.94439$$

$$\sigma_Y = \sqrt{\frac{\Sigma(Y)^2}{N} - \frac{(\Sigma Y)^2}{(N)^2}}$$

$$= 0.034330$$

$$p = \frac{\Sigma(XY)}{N} - \frac{(\Sigma X)}{(N)} \times \frac{(\Sigma Y)}{(N)} = 0.056194$$

$$r = \frac{p}{\sigma_X \sigma_Y} = 0.842 = \text{the correlation coefficient}$$

$$Y - \bar{Y} = r \frac{\sigma_Y}{\sigma_X} (X - \bar{X})$$

$$Y = 0.0149X + 0.0261$$

$$S_Y = \sigma_Y \sqrt{1 - r^2} = 0.0185$$

Probability level of significance of  $r = 0.99$



tions, as indicated in Table 1, yield the quantities required to determine the correlation coefficient, calculation of which is shown in Table 2. The use of a tabulating machine rather than a listing machine would make possible still further simplification of the calculations.

In order to effect the greatest economy of time, the possible contingencies likely to be encountered should be anticipated in the design of the cards for any particular study.

Table 3 lists some of the results of this preliminary study and Fig. 1 shows graphically the correlation between the FeO in the steel and the reciprocal of the carbon. The latter indicates the advantage of transformation of variable in order to obtain a linear relation. In the construction of this figure the average and limit lines were drawn in before the actual points were plotted. All of the tests used in this study were sufficiently near the same stage of the heat to be comparable. The correlations of the FeO in the steel with the ferrous iron in the slag and of the FeO in the steel with the total iron of the slag calculated to FeO show fair degrees of relationship. There is no statistically significant difference between these two correlation coefficients indicating no better relationship in the one case than in the other. The carbon FeO (steel) product increases with carbon and shows a moderate correlation coefficient. Very good correlations exist between the FeO in the steel and the reciprocal of the carbon, and between the ratio of the FeO in the slag to that in the steel and the basicity of the slag as indicated by the lime-silica ratio.

TABLE 3.—Results of Preliminary Correlations of Slag-metal Analyses from Plant E

ALL TESTS LATE IN HEAT

Variables		Number of Heats	Correlation Coefficient $r$	Probable Significance of $r$	Line of Regression (Average $Y$ )
$Y$	$X$				
FeO <sub>steel</sub> ; true slag FeO.		50	+0.315	0.98-0.99	FeO <sub>steel</sub> = 0.00465FeO <sub>slag</sub> + 0.109
FeO <sub>steel</sub> ; total slag Fe as FeO.....		50	+0.341	0.98-0.99	FeO <sub>steel</sub> = 0.00384FeO <sub>slag</sub> + 0.107
C · FeO <sub>steel</sub> ; C.....		59	+0.553	0.99+	C · FeO = 0.0591C + 0.0113
FeO <sub>steel</sub> ; 1/C.....		59	+0.842	0.99+	FeO <sub>steel</sub> = $\frac{0.0149}{C}$ + 0.0261
FeO <sub>slag</sub> , CaO FeO <sub>steel</sub> , SiO <sub>2</sub> .....		57	+0.860	0.99+	$\frac{\text{FeO}_{\text{slag}}}{\text{FeO}_{\text{steel}}} = 30.46 \frac{\text{CaO}}{\text{SiO}_2} - 16.36$

Discussion

F. G. NORRIS.—The nature of open-hearth data is such that we are forced to use the same methods in order to secure any degree of reliability in the results. I hope that it will be possible to have a complete description, either in the minutes of the meeting or by publication in some other manner, of the methods of calculation that have been used. Mr. Feters said that he wished he had a tabulating machine, but many of us do not even have a listing machine and therefore are interested in short-cut methods. The correlation coefficient Mr. Feters used is the usual product moment coefficient. Calculation requires the knowledge of the standard deviation of both variables and evidence that they both are under control. There is a short-cut method that I think would be of interest; this is the rank difference correlation. The same general conclusions can be drawn from each. A correlation of around 0.85 or 0.90 gives some degree of confidence in a linear relation such as has been shown. Values around 0.30 or 0.50 do not give much evidence of correlation.

## Slag-metal Relationships in the Basic Open-hearth Furnace

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(New York Meeting, February 1940)

IN the process of making steel in the open-hearth furnace the refining of the metal during the working period of the heat is largely accomplished through the agency of the slag. From the birth of the process until the present day steelmakers have recognized the importance of the slag in determining the composition of the metal and the quality of the product. The general relationships between slag composition and metal analysis have long been known, at least in a qualitative or approximate fashion. For examples, the iron oxide content of the slag is higher on lower carbon heats; the more basic slags are higher in iron oxide for a given carbon content; certain amounts of iron oxide and lime are required for phosphorus removal and a high lime-silica ratio is needed if the sulphur content of the metal is to be diminished. In recent years a number of quantitative relationships involving these and other variables have been developed through plant and laboratory studies by numerous investigators in this country and abroad.

The direct comparison of laboratory and open-hearth data involves the question of the degree to which each approaches the conditions of chemical equilibrium, a question which, from the open-hearth standpoint, we are scarcely yet in position to answer. And, although a considerable body of dependable equilibrium data has been obtained in the laboratory, this work has not yet been extended to cover the ranges of slag composition encountered in basic open-hearth practice. In the present study we shall not attempt to draw comparisons between data from the two sources; nor do we attempt to draw conclusions as to the approach to chemical equilibrium in the open-hearth furnace.

Many of the operating variables that are likely to be erratic or unrecorded during the earlier stages of the heat become more consistent and are more readily subject to observation and control during later stages. For example, undigested lime or ore gradually goes into solution, the rate of carbon drop levels off, and the temperature of the metal is brought under control. For these and other reasons a greater degree of self-consistency is likely to be found among data obtained during the

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Manuscript received at the office of the Institute Nov. 30, 1939. Issued as T.P. 1164 in METALS TECHNOLOGY, February 1940.

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later stages of the heat. The addition of a substantial amount of deoxidizer immediately erases any relationship between the iron oxide content of slag and metal, and for purposes of our study samples taken after deoxidation were excluded. This does not apply to the addition of a small amount of pig iron or spiegel as a reboiling agent. Such an addition often induces more intimate contact of slag and metal and samples taken from 20 to 40 min. after such an addition have been included.

The purpose of this investigation was to examine and correlate the relationships that exist between slag and metal during the final stages of the basic open-hearth process but prior to deoxidation; questions of equilibrium and of reaction rate will be left to subsequent papers.

### OPEN-HEARTH DATA

The complexity of the slag-metal system and the interdependence of the large number of variables associated with the process preclude the possibility of drawing broad generalizations from a small number of heats. For this reason the cooperation of a number of metallurgists, open-hearth operators and research workers was solicited, and these cooperators were asked to furnish data on the composition of slag and metal during the final stages of a large number of heats. The data requested were complete slag and metal analyses, the latter to be based upon samples taken by the so-called "bomb test" or closed spoon described by McCutcheon and Rautio,<sup>1</sup> and including the oxygen content of the metal. Samples were to be obtained immediately before deoxidation or final furnace additions or, for undeoxidized heats, before tapping.

Data were contributed by eight steel-producing companies, representing a total of 424 heats. Since certain heats were sampled more than once, the total number of metal samples amounted to 650, but some of these could not be grouped with the rest because of a too short lapse of time after a furnace addition. There remained 526 metal samples and a somewhat smaller number of slag analyses upon which the study could be based. These covered a range of carbon content from 0.02 to 1.02 per cent and represented a very great variety of steelmaking practices. Furnace sizes, bath depths, fuels and raw materials covered a wide range, for which the data were transmitted by some of the cooperators.

### STATISTICAL METHODS OF ANALYSIS

The examination of this mass of data to determine the relationships between the many composition variables proved to be no small task. Mere tabulation of the data would occupy about ten pages of *TRANSACTIONS*, which would be more than doubled by including values of the

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<sup>1</sup> References are at the end of the paper.

numerous ratios and "constants" that have been studied. Fortunately such a procedure is unnecessary. The data and the interrelationships of the many variables can be presented in certain cases as averages and standard deviations, in others as lines of regression and correlation coefficients. (See note at the end of the Summary.)

In the study of the variation of the factors from heat to heat and their relation to one another, various quantitative statistical measures of these variations and relations have been used. These measures, other than the well-known average (designated as  $\bar{X}$ ), may be briefly described in the following. The standard deviation, designated by  $\sigma$ , rigorously defined as the root-mean-square-deviation, is simply a measure of the spread or variation of any quantity about its arithmetic mean; it possesses certain very convenient algebraic properties of manipulation. In the case of any variable normally distributed about its average, limits of plus or minus twice the standard deviation may be expected to include 95 per cent of all values.

The "product moment correlation coefficient,  $r$ ," is a number that characterizes the degree to which two variables are linearly associated either by commonness of causation or because one is a linear function of the other. The values of this coefficient vary from  $-1$  through  $0$  to  $+1$ , the approaches to  $\pm 1$  indicating increasing degrees of relationship. If a value of  $+1$  or  $-1$  were obtained, the relation between the variables included would be that of an exact mathematical law with no variations. Tests are available by which we may determine the probable significance of a correlation coefficient or the measure of confidence to be placed in an observed correlation. In this study the correlations with a coefficient that would be likely to be obtained less than nine times out of ten have been indicated as less certain. The significance in any particular case increases with the number of samples from which the coefficient was obtained.

When two variables are linearly related, that fact can be represented graphically by a straight line. Such a line is referred to as a line of regression and its slope is a function of the correlation coefficient. Its equation may be calculated readily from  $r$ , the standard deviations, and the averages of the variables involved. When it is desired to express one variable in terms of another, this dependent variable is usually designated as  $Y$  and the independent variable as  $X$ . The equation of regression of  $Y$  on  $X$  minimizes the deviations in the vertical direction and hence for a given value of  $X$  gives the most probable value of  $Y$ . For this reason, the regression of  $Y$  on  $X$  with  $X$  as the independent variable has been used throughout this paper. For slight departures from linearity this method is still useful and gives the best straight-line relation possible for the points involved.

The application of statistical methods to the data available for this study required consideration of the metallurgical factors involved.



After a preliminary examination of various distributions of slag and metal analyses by plants, it was evident that a purely statistical treatment would require separation of the data by plants, since the usual tests to determine if all analyses represented random samples from the same system showed that they did not. The tests, however, do not represent random open-hearth operation but are the result of the grades of steel and the degree of control of slag and metal composition current in any particular plant. This investigation was primarily concerned with relations between variables, and, since no physicochemical reasons exist for expecting differences in these relations between plants, all data were combined for study. Restriction of the data by plants would have limited the number of tests available for the various subclassifications desired as well as limited the general applicability of the results obtained, and vastly increased the work of analysis. That this practice was justified will be evident from the discussion and figures following, which show the same trend and same relationships wherever the separation by plants has been made. The application of precise statistical tests for homogeneity to the series of correlation coefficients of Table 5 (the Chi square test described by L. H. C. Tippett<sup>2</sup>) do not indicate a completely homogeneous system by plants, but owing to the various ranges of composition represented the condition is much the same as though various ranges were studied in the same plant where lack of homogeneity of the correlations obtained would not be felt to restrict the general applicability of the results.

The analysis of the data is greatly facilitated by the use of modern card-punching, sorting, tabulating and multiplying machines. The details and limitations of the methods used were described in a previous paper<sup>3</sup> and represent an adaptation of the Mendenhall-Warren-Hollerith<sup>4</sup> correlation method, which was devised for educational studies.

Having made the decision to combine the data from all plants and to assume that all samples were representative of the same system of causes, it was necessary to make certain subclassifications of the data to eliminate the known large influence of carbon and to permit the development of the true relations existing among the several variables. Table 1 shows the carbon classifications used, the number of samples in each of the eight groups and the distribution by cooperating companies. Nine samples, which did not fit into any group, were omitted from the table and the studies.

The principal variables studied, along with the average value and standard deviation of each in each of the carbon groups, are listed in Table 2. The symbols and several of the quantities listed require special comment. The square brackets are used to designate concentrations in the metal, round parentheses in the slag, and all concentrations are expressed as percentage by weight. The quantity  $[\text{FeO}]_M$  is obtained



TABLE 1.—*Distribution of Samples by Plants*

Carbon Range, Per Cent..	0.020- 0.045	0.046- 0.055	0.056- 0.065	0.066- 0.085	0.086- 0.115	0.116- 0.180	0.19- 0.31	0.39- 0.51	Total
Group No.....	1	2	3	4	5	6	7	8	
Plant									
A.....	13	18	20	20	11	3	16	17	118
B.....			5	6	8	14	15	1	49
C.....	21	46	52	27	4				150
D.....	24	25	12	13	1		1		76
E.....				7	26	21			54
G.....	1		6	4	6	2			19
J.....				3	9	3	9		24
M.....					4	9	14		27
Total.....	59	89	95	80	69	52	55	18	517

directly from the alumina content of aluminum-killed samples taken in the covered mold. It represents the total oxygen content of the metal as determined by this method. The symbol (FeO) represents the percentage of ferrous oxide in the slag. (FeO)<sub>Total</sub> is the result obtained by converting the total iron content of the slag stoichiometrically to FeO; it is equivalent to (FeO) + 0.9(Fe<sub>2</sub>O<sub>3</sub>).

The meaning of most of the ratios considered is fairly evident. In addition to the usual lime-silica ratio the corrected ratio, *R*, has been included, defined in terms of weight percentages as:

$$R = \frac{(\text{CaO})}{(\text{SiO}_2) + 0.634(\text{P}_2\text{O}_5)}$$

This method of correcting for phosphorus assumes that one mol of P<sub>2</sub>O<sub>5</sub> can combine with half again as much lime as one mol of SiO<sub>2</sub>; it seems more reasonable to add this to the silica than to subtract it from the lime.

Several so-called manganese constants were calculated. These are not necessarily equilibrium constants, although they would be if equilibrium were reached and if the solutions were ideal. For our present purposes they are best regarded as mere ratios whose variations with other slag and metal variables are to be investigated. The three ratios employed are defined as follows:

$$K_{\text{Mn}}(1) = \frac{(\text{MnO})}{(\text{FeO})[\text{Mn}]}$$

$$K_{\text{Mn}}(2) = \frac{(\text{MnO})}{(\text{FeO})_{\text{Total}}[\text{Mn}]}$$

$$K_{\text{Mn}}(3) = \frac{(\text{MnO})}{[\text{FeO}]_M[\text{Mn}]}$$

TABLE 2.—Averages and Standard Deviations of Variables in the Several Carbon Ranges

Group No.	1		2		3		4		5		6		7		8	
	$\bar{X}$	$\sigma$	$\bar{X}$	$\sigma$	$\bar{X}$	$\sigma$	$\bar{X}$	$\sigma$	$\bar{X}$	$\sigma$	$\bar{X}$	$\sigma$	$\bar{X}$	$\sigma$	$\bar{X}$	$\sigma$
Variable:																
1. $[\text{FeO}]_M$	0.33	0.063	0.28	0.056	0.27	0.057	0.23	0.058	0.17	0.039	0.14	0.027	0.11	0.025	0.085	0.046
2. $[\text{C}]_M \times [\text{FeO}]_M$	0.0133	0.0031	0.0142	0.0028	0.0167	0.0033	0.0177	0.0043	0.0174	0.0033	0.0189	0.0041	0.0242	0.0064	0.0334	0.0064
3. $[\text{Mn}]_M$	0.097	0.050	0.12	0.047	0.15	0.049	0.15	0.053	0.16	0.071	0.15	0.064	0.22	0.111	0.34	0.099
4. $(\text{FeO})$	24.2	5.02	21.8	3.50	19.9	3.38	18.4	3.56	13.1	3.38	12.5	3.13	13.1	3.07	9.9	2.93
5. $(\text{FeO})$	9.3	2.11	9.2	1.92	8.5	2.55	7.6	2.07	5.5	2.24	5.6	1.76	5.0	2.57	5.8	2.26
6. $(\text{FeO})_{\text{Total}}$	32.5	5.26	30.0	4.47	27.6	4.47	25.4	4.91	18.3	4.86	17.7	4.34	18.1	4.91	14.8	3.94
7. $(\text{FeO})/(\text{FeO})$	0.40	0.112	0.43	0.089	0.42	0.119	0.42	0.111	0.43	0.131	0.48	0.124	0.42	0.136	0.47	0.188
8. $(\text{CaO})/(\text{SiO}_2)$	3.26	0.598	3.36	0.687	3.44	0.820	3.51	0.587	3.06	0.938	3.56	0.754	3.84	1.208	2.86	0.561
9. $R$	2.94	0.490	3.04	0.545	3.07	0.625	3.11	0.742	2.68	0.687	2.94	0.749	3.19	1.028	2.57	0.398
10. $(\text{FeO})/[\text{FeO}]_M$	74.6	15.37	79.85	21.1	74.34	18.3	81.20	27.1	73.20	20.95	92.55	29.7	117.5	32.75	138.6	83.8
11. $(\text{FeO})_{\text{Total}}/[\text{FeO}]_M$	101.2	19.5	110.9	28.3	103.2	22.2	112.6	34.7	105.0	28.3	131.9	40.7	167.0	47.4	203.6	113.2
12. $K_{\text{Mn}}(1)$	3.46	0.94	3.21	0.73	3.04	0.76	2.98	0.91	3.96	1.46	3.50	1.36	2.57	1.09	4.18	1.32
13. $K_{\text{Mn}}(2)$	2.57	0.74	2.35	0.60	2.21	0.42	2.18	0.68	2.83	0.95	2.40	0.90	1.90	0.86	2.79	0.93
14. $K_{\text{Mn}}(3)$	258	82	248	69	225	66	233	73	274	89	294	91	282	100	523	206
15. $(S)/[S]_M$	4.75	1.16	4.80	1.35	5.33	1.54	5.91	1.92	4.47	1.95			5.18	2.53	6.97	1.38

## FACTORS DEPENDENT UPON CARBON

Inspection of Table 2 confirms the well-known fact that as we progress from lower to higher carbon ranges, certain variables progressively

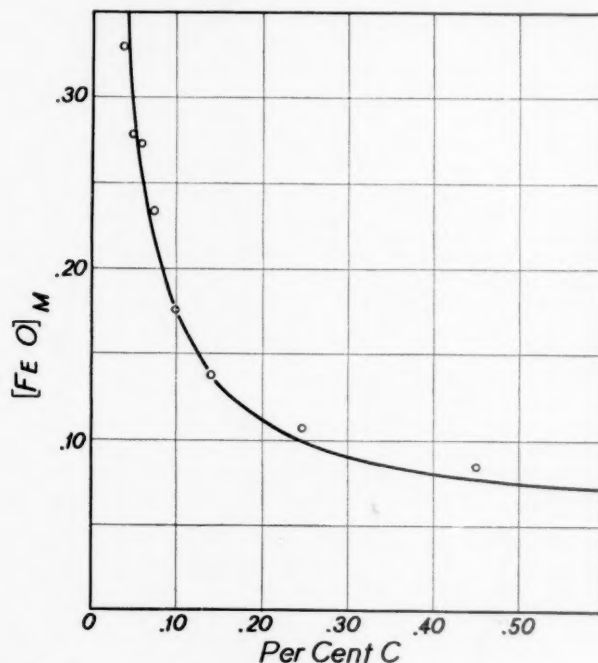


FIG. 1.—AVERAGE RELATION BETWEEN  $[\text{FeO}]_M$  AND CARBON IN EIGHT GROUPS. DATA FROM ALL PLANTS.

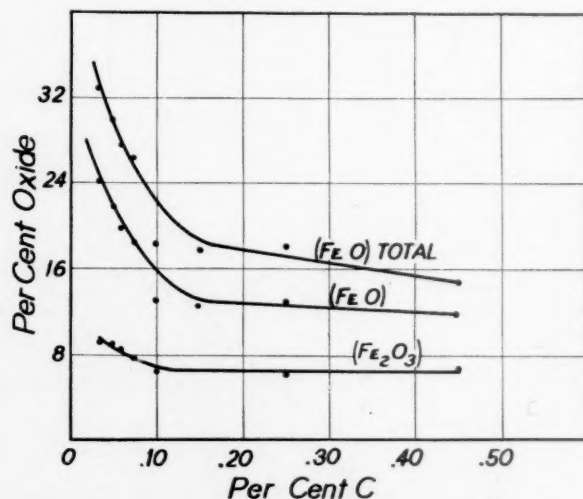


FIG. 2.—AVERAGE OXIDE OF SLAG AS FUNCTION OF CARBON, DATA FROM ALL PLANTS.

decrease and others increase. As would be expected, an increase in carbon is attended by a decrease in the iron oxide content of slag and metal. In general, it is also associated with an increase in residual

manganese, although no causal relation is implied. These results are shown graphically in Figs. 1 to 3, in which the plotted points represent average values for the eight carbon groups. The ratio of the two iron oxides in the slag (item 7, Table 2) is independent of carbon but the

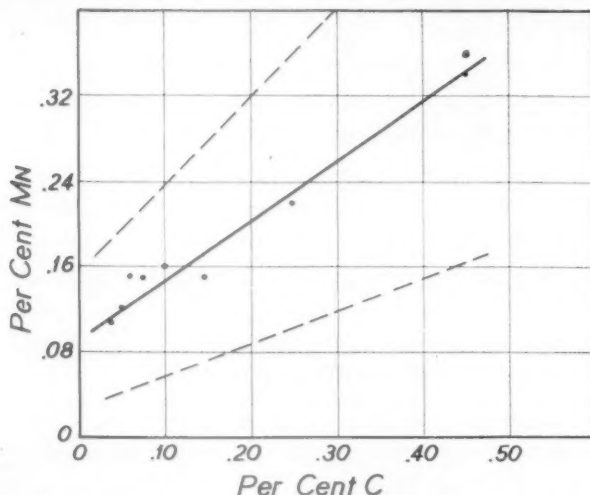


FIG. 3.—RELATION BETWEEN RESIDUAL MANGANESE AND CARBON, DATA FROM ALL PLANTS.

Limits shown are approximately  $2\sigma$ .

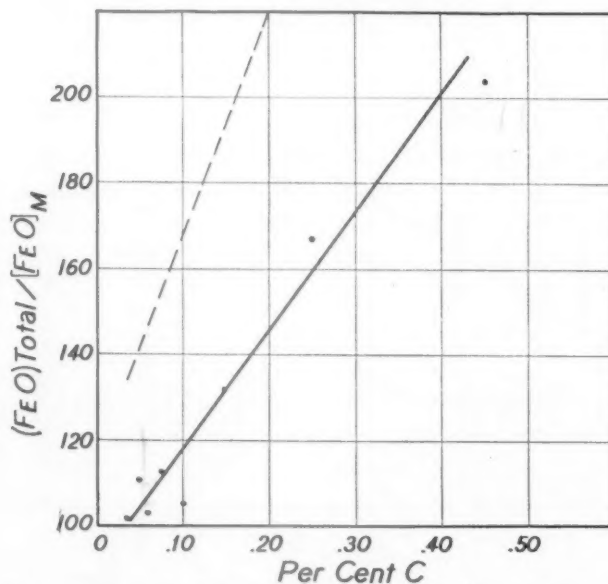


FIG. 4.—AVERAGE DISTRIBUTION RATIO  $(\text{FeO})_{\text{Total}}/[\text{FeO}]_M$  AS FUNCTION OF CARBON, DATA FROM ALL PLANTS.

Upper  $2\sigma$  limit is shown; lower limit is below edge of graph.

distribution of iron oxide between slag and metal (items 10 and 11) shows a marked dependence upon carbon content. The average ratio of total iron oxide in the slag to iron oxide in the metal is plotted against carbon in Fig. 4. The limit lines shown in Figs. 3, 4 and 5 have been

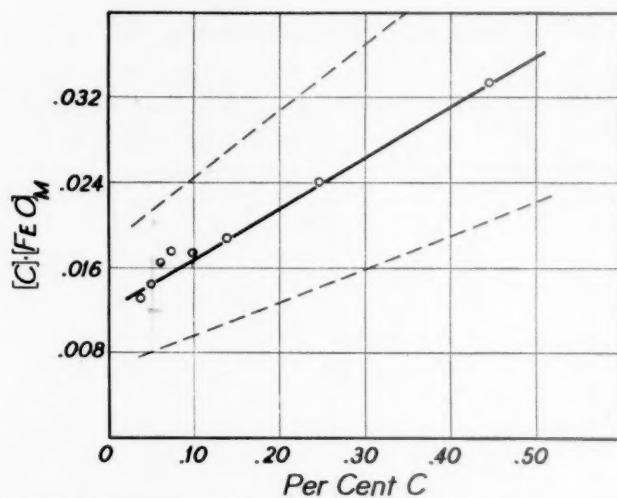


FIG. 5.—VARIATION OF AVERAGE  $[C] \cdot [FeO]_M$  PRODUCT WITH CARBON, ALL PLANTS. Limits shown are approximately  $2\sigma$ .

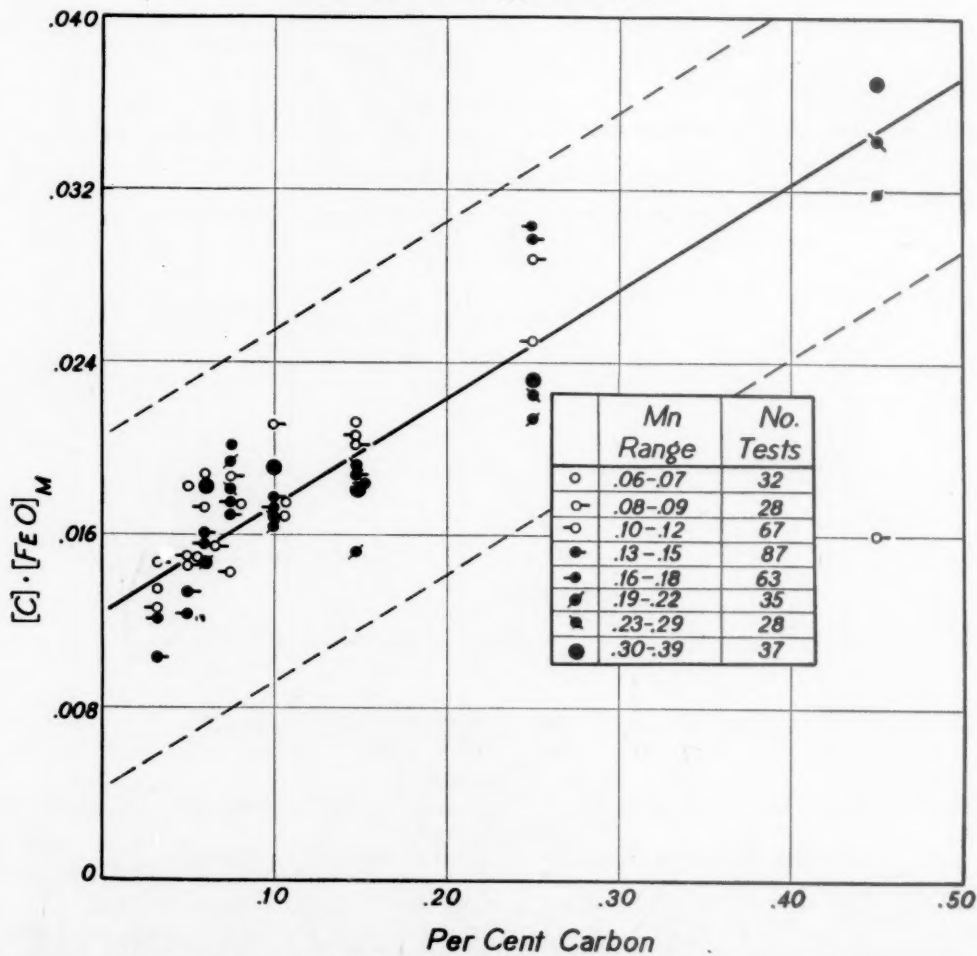


FIG. 6.—VARIATION OF PRODUCT  $[C] \cdot [FeO]_M$  WITH CARBON FOR MANGANESE SUBGROUPS.  $2\sigma$  limits shown.



estimated from the standard deviations of the variables within each of the carbon groups and represent approximate  $2\sigma$  limits within which most of the individual points might be expected to fall.

The product carbon times iron oxide in the metal has often been supposed a constant. The data of Table 2, which are plotted in Fig. 5, indicate clearly that under the conditions here considered this product is dependent upon the carbon content itself. Again the points plotted are the averages for the carbon groups, the dotted lines represent approximate  $2\sigma$  limits; i.e., the limits within which lie approximately 95 per cent of all points.

Since it was shown in Fig. 3 that for the entire group of heats an increase in residual manganese was associated with an increase in carbon, the question naturally arises, is the marked trend of Fig. 5 properly associated with carbon content or is it due to the effects of manganese upon one or both of the reactants? In order to answer this question the cards of each carbon group were subdivided into several manganese subgroups. In Fig. 6 the product  $[C] \times [\text{FeO}]_M$  is again plotted against carbon, using a different symbol for each of the manganese subgroups. Careful inspection of this figure will show that the line, which is the regression line of Fig. 5, fits each of the manganese subgroups about equally well. Within any one of the carbon groups there is no significant relationship between the manganese content and the  $[C] \times [\text{FeO}]_M$  product.

Among the variables listed in Table 2, those showing little or no dependence upon carbon content are: 7, the ratio  $(\text{Fe}_2\text{O}_3)/(\text{FeO})$ ; 8 and 9, the basicity ratios; 12, 13 and 14, the manganese constants. Among the last there is an increase in the highest carbon group, which may, however, be related to the slightly lower basicity in this group. The sulphur distribution ratio, 15, shows an erratic increase with increasing carbon, indicating that a closer relationship with other factors should be sought.

#### CORRELATIONS WITHIN THE CARBON GROUPS

If a given variable is strongly affected by variations in carbon content, it is clear that its relationship to other variables can best be studied in a group within which the carbon content is constant. Lacking sufficient heats to establish large groups at exactly constant carbon, the same purpose can be served by dividing the data into the narrow ranges represented in Table 2 and studying the interrelationships within each group.

In order to determine whether a relationship exists between two variables the correlation coefficients have been computed for a number of pairs for which some degree of relationship might be expected. These coefficients are shown for each carbon group in the columns headed  $r$  in Table 3. The alternate columns, marked  $N$ , give the number of values

TABLE 3.—Summary of Correlation Coefficients in the Several Carbon Ranges

Group No.....		1		2		3		4		5		6		7		8	
Carbon, Per Cent.....		0.020-0.045C		0.046-0.055C		0.056-0.065C		0.066-0.085C		0.086-0.115C		0.116-0.180C		0.19-0.31C		0.39-0.51C	
N	r	N	r	N	r	N	r	N	r	N	r	N	r	N	r	N	r
Variables																	
X		Y															
1. [C] <sub>M</sub>	52	0.42	81	0.21	93	(0.03)	80	0.19	68	(-0.02)	52	(0.12)	53	0.41	17	0.34	
2. [Mn] <sub>M</sub>	45	(-0.14)	75	(-0.12)	90	(0.11)	77	0.25	64	(0.05)	41	(0.03)	39	(0.08)	18	(0.06)	
3. R	45	(-0.19)	74	0.39	90	0.34	74	0.67	55	0.75	38	0.88	30	0.50	17	0.72	
4. R	45	(0.04)	74	0.49	90	0.52	74	0.61	55	0.80	38	0.84	30	0.55	17	0.75	
5. R	45	0.60	74	0.43	90	0.51	74	(0.19)	55	(0.21)	38	(-0.22)	30	0.36	17	(0.21)	
6. CaO/SiO <sub>2</sub>	45	(0.21)	74	0.43	90	0.45	74	0.59	55	0.57	38	0.75	30	0.60	17	0.79	
7. CaO/SiO <sub>2</sub>	45	(0.23)	75	0.31	90	0.52	77	0.55	63	0.59	41	0.74	40	0.66	18	0.83	
8. R	45	(0.06)	74	0.33	90	0.37	74	0.51	55	0.60	38	0.74	30	0.43	17	0.69	
9. R	45	(0.20)	75	0.37	90	0.58	77	0.53	63	0.62	41	0.76	40	0.68	18	0.88	
10. R	45	(0.07)	75	0.25	90	-0.77	77	(0.11)	64	0.32	41	(0.20)	39	0.49	18	(0.07)	
11. (FeO <sub>2</sub> )	45	(0.08)	75	(0.16)	90	(0.17)	77	0.37	64	0.47	41	0.34	39	0.40	18	(0.19)	
12. (Fe <sub>2</sub> O <sub>3</sub> )	45	0.46	75	0.48	90	0.40	74	0.23	55	0.29	38	0.29	30	0.58	18	(0.11)	
13. (FeO <sub>2</sub> )	45	0.51	75	0.50	90	0.50	77	0.35	63	0.36	41	0.47	40	0.60	18	(0.14)	
14. [Mn] <sub>M</sub>	45	(0.05)	75	0.38	90	(0.07)	74	(-0.03)	55	(0.11)	38	(-0.15)	30	(-0.19)	18	-0.52	
15. [Mn] <sub>M</sub>	45	(-0.06)	75	(0.13)	90	(-0.17)	77	-0.86	63	(-0.08)	41	-0.32	40	-0.30	18	-0.60	
16. K <sub>Mn</sub> (1)	45	(0.16)	75	-0.24	90	(0.08)	74	-0.42	55	-0.50	38	-0.71	30	-0.55	18	-0.37	
17. R	45	(-0.01)	74	-0.24	90	-0.43	74	-0.58	55	-0.63	38	-0.79	30	-0.44	17	-0.35	
18. R	45	(-0.20)	74	-0.25	90	-0.74	74	-0.56	55	-0.74	38	-0.84	30	-0.48	17	-0.36	
19. R	45	(-0.05)	74	(0.11)	90	(-0.10)	74	(-0.12)	55	-0.31	38	-0.38	30	(-0.19)	17	(0.32)	
20. CaO/SiO <sub>2</sub>	27	0.84	39	0.48	56	0.72	50	0.79	31	0.74			26	0.77	16	0.61	
R	27	0.83	39	0.91	56	0.78	50	0.78	31	0.78			26	0.80	16	0.61	

\* Correlation coefficients in parentheses have a probable significance less than 0.90.

used in computing  $r$ . Because of the incompleteness of some of the data,  $N$  is in general smaller than the total number in each group of Table 1. The probable significance of each correlation was read from Fisher's<sup>5</sup> tables, and where this was less than 0.90 the coefficient is placed in parenthesis. Where this occurs in the majority of the groups, it may be concluded that no actual relationship exists, that the relation has been hidden by its interrelation to some other factor, that there is such a marked departure from linearity as to diminish the coefficient greatly, or that the range represented by one of the variables is insufficient to establish it. Thus there is no apparent relationship between manganese and iron oxide in the metal. Similarly, at low carbon there is a low and contradictory correlation between manganese and the distribution ratios  $(\text{FeO})/[\text{FeO}]_M$  and  $(\text{FeO})_{\text{Total}}/[\text{FeO}]_M$ . At higher carbon content a definite negative correlation exists. It is evident also that among the three manganese constants only the first two are related to basicity of the slag.

For the rest it can be said that actual relationships exist between the pairs of variables listed in the table. The relationship becomes the more definite the greater the number of points considered and the higher the correlation coefficient. For the values of  $r$  not enclosed in parentheses the probability that the relationship is purely fortuitous is less than 1 in 10.

The data of Tables 2 and 3 enable us to choose between two alternative methods of expressing almost the same thing; i.e., between the two very closely related variables  $(\text{FeO})$  and  $(\text{FeO})_{\text{Total}}$ . It is found that the use of the latter gives slightly more consistent results. In Table 2 the percentage deviations in item 11 are slightly smaller than in item 10. In Table 3 it is evident that the two distribution ratios are both related to the lime-silica ratio as shown in lines 6 and 7 and the correlation coefficients are about equally good. Using the corrected lime-silica ratio in lines 8 and 9, it is found that the quantity  $(\text{FeO})_{\text{Total}}$  affords a distinctly higher correlation. Similarly, when the two manganese constants  $K_{\text{Mn}}(1)$  and  $K_{\text{Mn}}(2)$  are compared, it is found that the latter, which involves  $(\text{FeO})_{\text{Total}}$  is more consistent and more closely related to slag basicity than the former, which involves only ferrous oxide. It is concluded, therefore, that  $(\text{FeO})_{\text{Total}}$  is a somewhat more consistent measure of the oxidizing power of the slag than is  $(\text{FeO})$ .

#### LINE OF REGRESSION WITHIN CARBON GROUPS

Having shown that certain correlations actually exist, it remains to determine quantitatively the nature of the relationships. It is convenient to do this by plotting the lines of regression of one variable upon the other. This represents the average value of one variable, which we may call  $Y$ , at any value of the other variable,  $X$ , within the

range of experimental points. The calculation is made from the same mechanical tabulation that was employed in obtaining the correlation

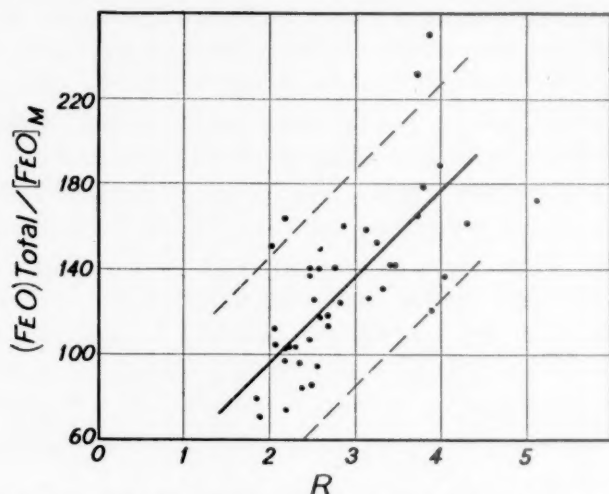


FIG. 7.—SCATTER DIAGRAM AND REGRESSION LINE OF DISTRIBUTION RATIO AS FUNCTION OF BASICITY.

Group 6 tests only (0.116 to 0.180 per cent C).  $2\sigma$  limits shown.

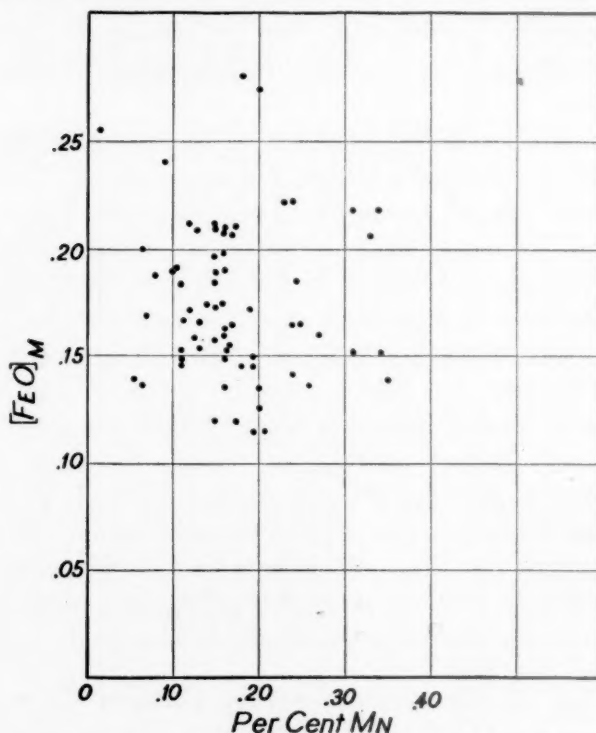


FIG. 8.—SCATTER DIAGRAM ILLUSTRATING LOW CORRELATION COEFFICIENT: FeO IN METAL AGAINST RESIDUAL MANGANESE.

Group 5 (0.086 to 0.115 per cent C).

coefficients. If the coefficient is high, the line affords an accurate representation of the average of the data. If the coefficient is very low,

the line becomes horizontal, indicating no variation of the average  $Y$  within the range of  $X$  considered.

Examples of high and low correlation coefficients are shown in Figs. 7 and 8, respectively. Fig. 7 shows the distribution ratio of iron oxide as a function of slag basicity in group 6. Since the line is calculated mechanically, it is obviously unnecessary to plot the points, but these are shown in order to illustrate the scatter to be expected of 41 points with a correlation of 0.76. Fig. 8 shows the iron oxide and manganese in the metal in group 5. Here are 64 points with a correlation of 0.05,

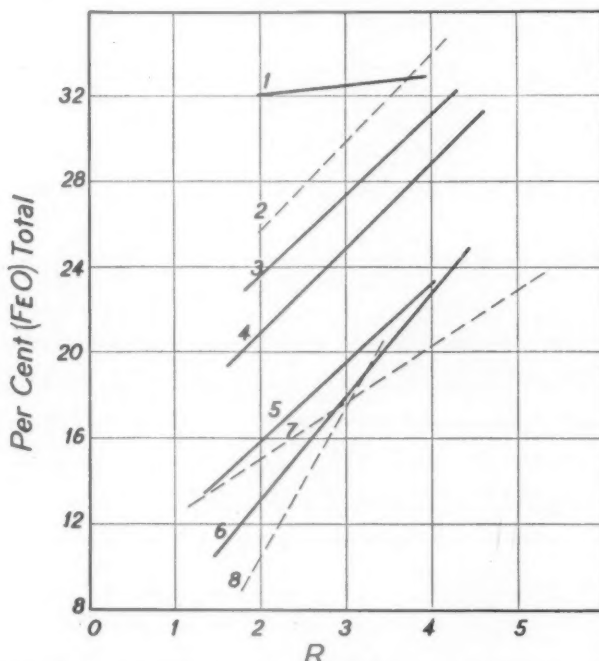


FIG. 9.—REGRESSION LINES OF  $(\text{FeO})_{\text{Total}}$  AGAINST BASICITY. Numbers refer to carbon groups.

and it is apparent that no sloping line will represent the data; i.e., there is no variation in the average  $[\text{FeO}]_M$  within this range of manganese.

It will be convenient to consider most of the variables as functions of the basicity ratio  $R$ . Lines of regression for total iron oxide of the slag against  $R$  are shown in Fig. 9. There is a fair degree of uniformity in the slopes of the lines and a clear trend to lower oxide in the higher carbon ranges. In this figure and others of a similar nature following, the limits within which the individual tests would fall have been omitted for clarity and to avoid any confusion incident upon visual comparison of the limits of one group with the regression line of another. A regression line is calculated from an appreciable number of tests and the limits about a regression line within which a second regression line need occur to be representative of the same "universe" are much narrower than



the limits of individual points. Such comparisons have been made, however, based on an adaptation of Shewhart's<sup>6</sup> control-chart methods,

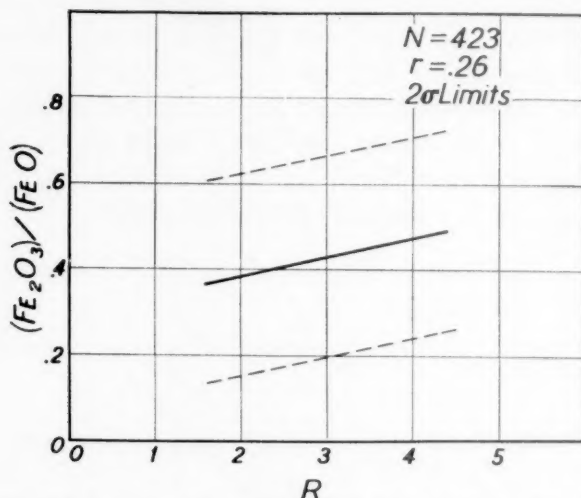


FIG. 10.—REGRESSION LINE AND LIMITS OF RATIO  $(\text{Fe}_2\text{O}_3)/(\text{FeO})$  IN SLAG AS FUNCTION OF BASICITY.

and although too detailed to be included, their indication has been considered in the drawing of conclusions. In Fig. 9 the higher carbon

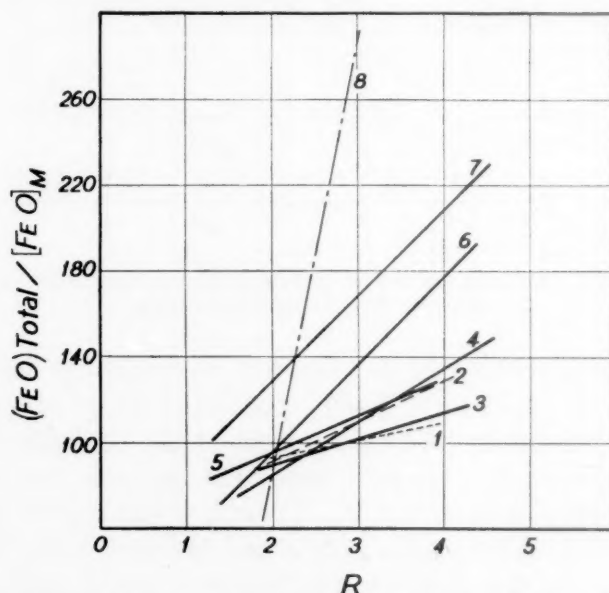


FIG. 11.—REGRESSION LINES OF DISTRIBUTION RATIO  $(\text{FeO})_{\text{Total}}/[\text{FeO}]_M$  AGAINST BASICITY.

Numbers refer to carbon groups.

groups 6, 7 and 8 are substantially the same but each of the lower carbon groups is significantly different from its neighbors. Any such consistent indication of a trend with some variable (in this case carbon)

further increases the probability of a significant difference over that which would be obtained by a comparison of any two succeeding groups.

The ratio of ferric to ferrous oxide in the slag was shown to be independent of carbon (Table 2), hence grouping is unnecessary and all of

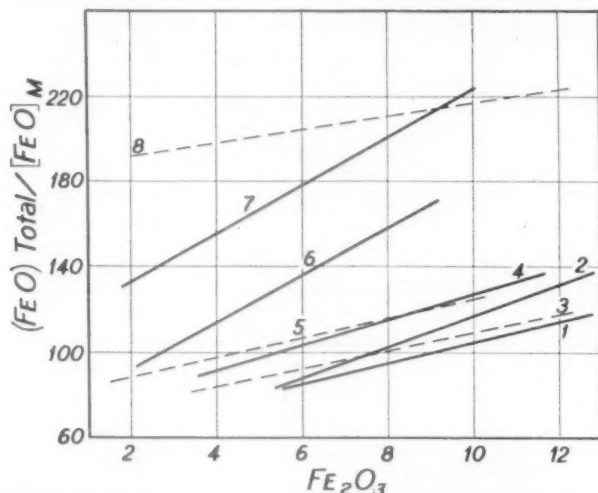


FIG. 12.—REGRESSION LINES OF  $(\text{FeO})_{\text{Total}}/[\text{FeO}]_M$  AGAINST  $(\text{Fe}_2\text{O}_3)$ .  
Numbers refer to carbon groups.

the values of this ratio can be represented on a single plot (Fig. 10). The correlation coefficient is only 0.26 and the scatter is very wide.

The distribution ratio  $(\text{FeO})_{\text{Total}}/[\text{FeO}]_M$  is shown as a function of  $R$  in Fig. 11. The effect of slag basicity evidently increases markedly with

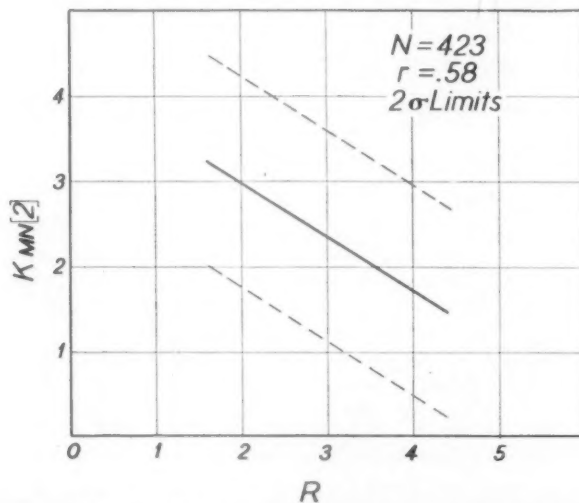


FIG. 13.—REGRESSION LINE AND LIMITS OF MANGANESE CONSTANT  $K_{\text{Mn}}(2)$  AGAINST BASICITY  $R$ .

increasing carbon content. The extremely steep slope in group 8 should be regarded with caution on account of the limited number of points involved in this group.

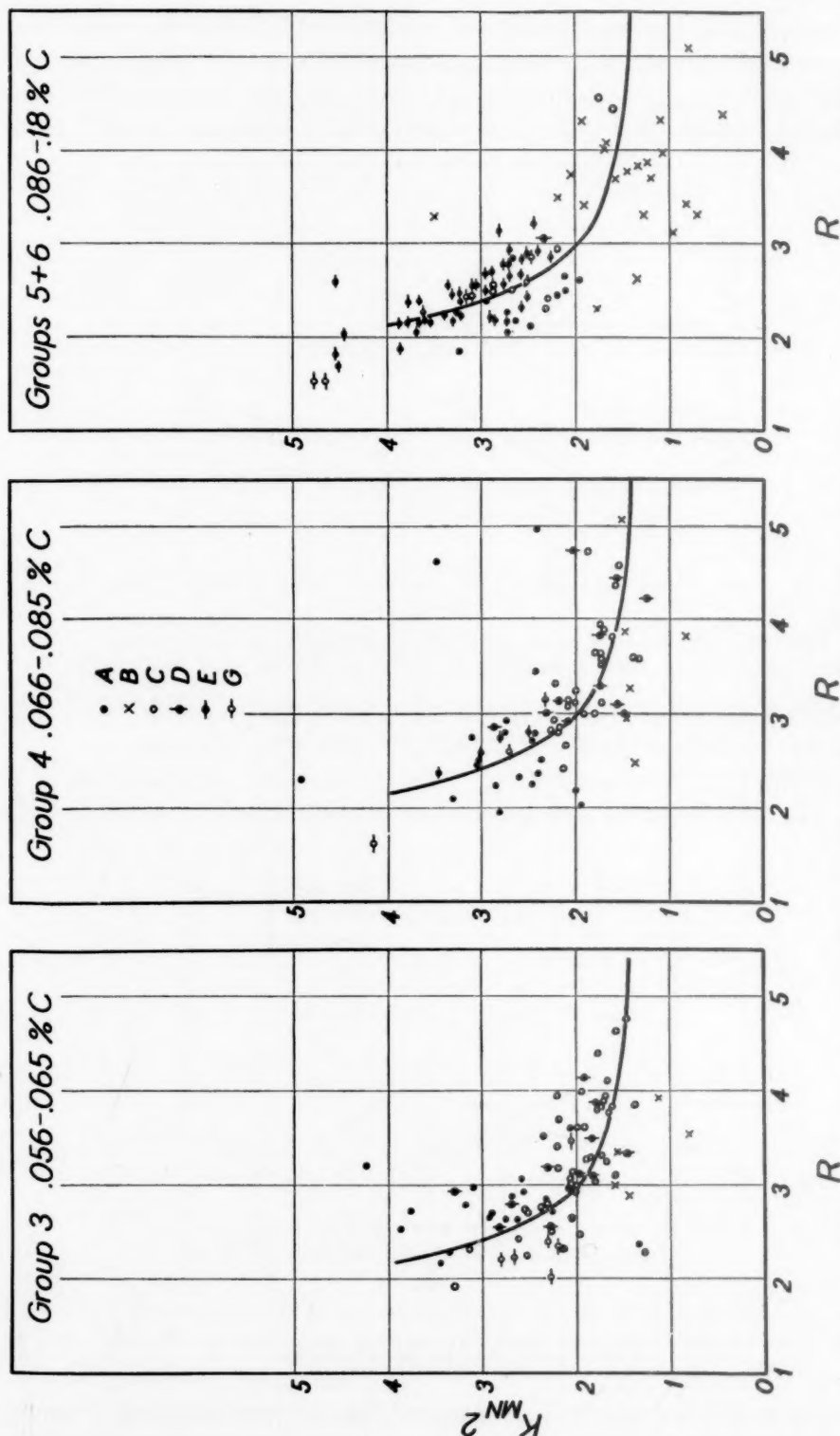


FIG. 14.—SCATTER DIAGRAM OF MANGANESE CONSTANT  $K_{Mn(2)}$  AS FUNCTION OF BASICITY FOR FOUR CARBON GROUPS. Same curve has been drawn through each group.

The relationship between the distribution ratio and the ferric oxide of the slag is shown in Fig. 12, and it will be noted that the lines all slope upward. There are two possible interpretations of this behavior. The first would be that the  $\text{Fe}_2\text{O}_3$  increases the total iron of the slag

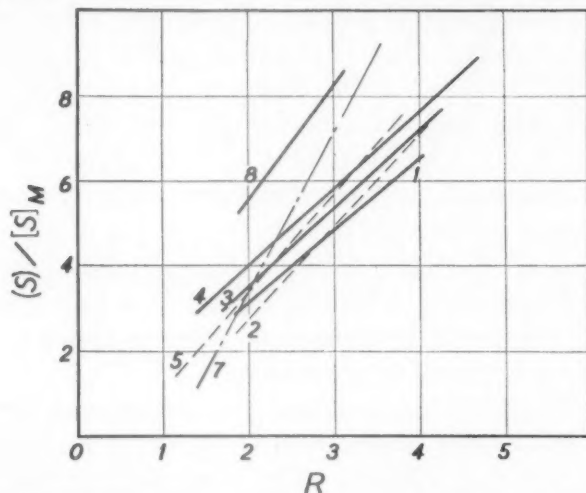


FIG. 15.—REGRESSION LINES OF SULPHUR DISTRIBUTION RATIO  $(S)/[S]_M$  AS FUNCTION OF BASICITY.

Numbers refer to carbon groups.

more than it affects the  $\text{FeO}$  in the metal, thereby indicating that its oxidizing effect upon the metal is less than that of the same amount of iron in the form of  $\text{FeO}$ . The second is that both of the variables increase with increasing basicity and that there is not necessarily any independent relationship between them.

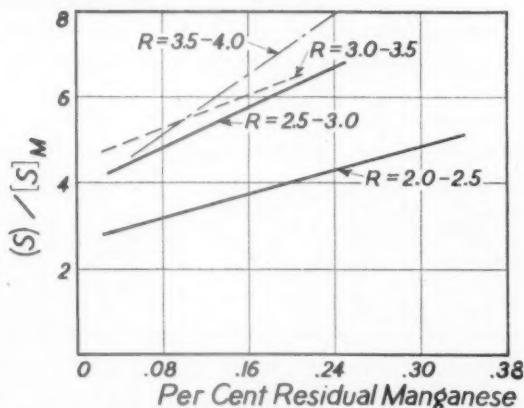


FIG. 16.—VARIATION OF RATIO  $(S)/[S]_M$  WITH RESIDUAL MANGANESE.

Including data up to 0.18 per cent carbon only. Lines represent four ranges of basicity.

The relation between the manganese constant  $K_{\text{Mn}}(2)$  and the basicity ratio is shown in Fig. 13. It was shown in Table 2 that there is no consistent variation of this constant with carbon and for this reason all points are included in Fig. 13. The relationship is examined more

critically in Fig. 14, which includes the data of groups 3, 4, 5 and 6 with symbols designating the source of each point. Here the line of regression is not the best line that can be drawn through the points; the curved line fits the data more convincingly and provides the explanation of the wide scatter in the previous graph. Where the actual relationship is curvilinear it is evident that a complete linear correlation could be obtained only by breaking down the data into smaller groups within which the relationship might be considered rectilinear. It is of interest that the curved lines drawn through the three graphs of Fig. 14 are in reality all the same line. This corroborates the previous conclusion that the manganese constant is independent of the carbon.

The distribution of sulphur between slag and metal is shown in Fig. 15 as a function of basicity. There is evidently a slight increase in the desulphurizing ratio as we progress from lower to higher carbons, but the main effect lies in the basicity of the slag.

Correlations between the residual manganese and the sulphur distribution ratio for various constant-basicity groups from 0.02 to 0.18 per cent carbon are listed in Table 4. The lines of regression corresponding to these correlation coefficients (Fig. 16) show the effects of both the manganese and the basicity on the desulphurization. The improvement in this ratio with increasing manganese as well as with higher basicity is evident, although the major role of the basicity is apparent.

TABLE 4.—*Variation of Sulphur Distribution Ratio with Residual Manganese and with  $K_{Mn}(2)$*   
ALL PLANTS, CARBON GROUPS 1 TO 6 INCLUSIVE

Number of Tests	Residual Manganese			(S)/[S] <sub>M</sub>		Correlation
	Basicity	$\bar{X}$	$\sigma$	$\bar{Y}$	$\sigma$	
58	2.00–2.49	0.180	0.078	3.94	1.40	0.41
59	2.50–2.99	0.139	0.057	5.54	1.48	0.45
47	3.00–3.49	0.118	0.047	5.65	1.30	0.35
22	3.50–3.99	0.143	0.047	6.21	1.51	0.56
	$K_{Mn}(2)$					
44	2.00–2.49	2.79	0.69	4.30	1.36	–0.17
59	2.50–2.99	2.55	0.68	5.54	1.48	0.31
47	3.00–3.49	2.26	0.67	5.65	1.30	0.33
22	3.50–3.99	1.90	0.54	6.21	1.51	0.55

Table 4 shows also the correlation coefficients between the manganese constant  $K_{Mn}(2)$  and the sulphur distribution ratio (S)/[S]<sub>M</sub> for the same constant basicity groups as used in the manganese investigation noted above. It was thought that the decrease of the manganese constant



and the increase of the sulphur distribution ratio with increasing temperature might result in negative correlations, but except for the lowest basicity group, the coefficient of which is not significant, the manganese constant definitely increases to some degree as the sulphur ratio increases. There are two possible interpretations of this trend: (1) that both ratios are influenced in the same direction by a third factor, such as  $(\text{FeO})$ ; (2) that an increase in the  $\text{MnO}$  content of a slag actually increases its basicity and that a ratio in which the equivalent  $(\text{MnO})$  is added to  $(\text{CaO})$  would be a more useful measure of slag basicity than the ratio  $R$ .

#### CONSIDERATION OF DATA BY PLANTS

A considerable number of correlations have been worked out for the data of the individual cooperators, and the results are shown in Table 5.

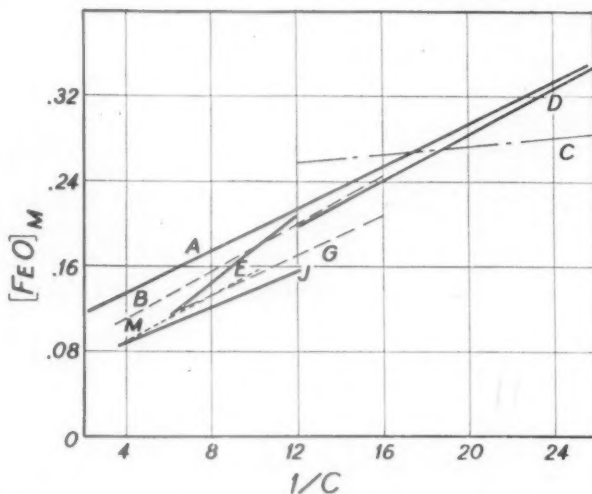


FIG. 17.—LINES OF REGRESSION OF IRON OXIDE IN METAL AGAINST RECIPROCAL CARBON FOR EACH PLANT.

These correlations cover the entire range of carbon content, and the coefficients of any relationship that is affected by carbon may be expected to appear low in this tabulation. This is particularly true for plant A, whose data covered the entire carbon range under consideration, and to a lesser degree for plant B, whose range was nearly as great. It is for this reason also that the coefficients for items 3 to 9 in Table 5 tend to run lower than for the corresponding items in Table 3 except for those plants whose carbon ranges are narrow.

Items 1 and 2 involving carbon and iron oxide in the metal show very good correlations for all except plant C, where the carbon range was rather limited. Item 1 may be cited as an example of what to do when the normal relationship between two variables is curvilinear in nature and as such not subject to treatment by the ordinary methods of correlation. Such transformations of variables by reciprocal or

TABLE 5.—Correlation Coefficients by Plants, All Carbon Ranges<sup>a</sup>

Plants.....	A		B		C		D		E		G		J		M	
	N	r	N	r	N	r	N	r	N	r	N	r	N	r	N	r
Variables																
X		Y														
1. 1/C	119	0.77	49	0.72	142	0.20	73	0.84	54	0.95	19	0.97	26	0.85	28	0.83
2. [C]	122	0.86	49	0.58	136	(0.11)	59	0.70	54	0.67	19	0.66	25	0.97	28	0.77
3. R	121	0.56							52	0.63						
4. R	121	0.62	49	0.26	136	0.23			52	0.73						
5. CaO/SiO <sub>2</sub>	121	0.19	49	0.27	137	0.25	51	0.55	52	0.63	19	0.57	25	(0.17)		
6. R	119	(0.10)	49	(-0.20)	143	-0.56	51	-0.70	51	-0.75	19	-0.70				
7. R	119	0.46	49		133	0.96	32	0.88	28	0.65	28	0.65				
8. CaO/SiO <sub>2</sub>	{ 110	0.21			116	0.64	27	0.75			27	0.82	16	0.79		
9. R	{ 48 <sup>b</sup>	0.57														

<sup>a</sup> Coefficients in parentheses are significant to a probability less than 0.9.<sup>b</sup> Including only heats with 0.020 to 0.065 per cent C.

logarithmic functions in order to obtain straight-line relationships permit the use of standard methods.

The lines of regression of  $[\text{FeO}]_M$  on  $1/[\text{C}]$  for each of the eight plants are plotted in Fig. 17. The remarkable agreement among the eight lines and the high values of seven of the eight correlation coefficients establish the average relationship between these two variables with considerable accuracy. This relationship is obviously similar to that expressed by the curve of Fig. 1 and the average line drawn through the points of Fig. 5, all of which will be discussed in a later paragraph.

The data of plant A cover a sufficient range of carbon to warrant the separate consideration of their carbon-iron oxide product as a function

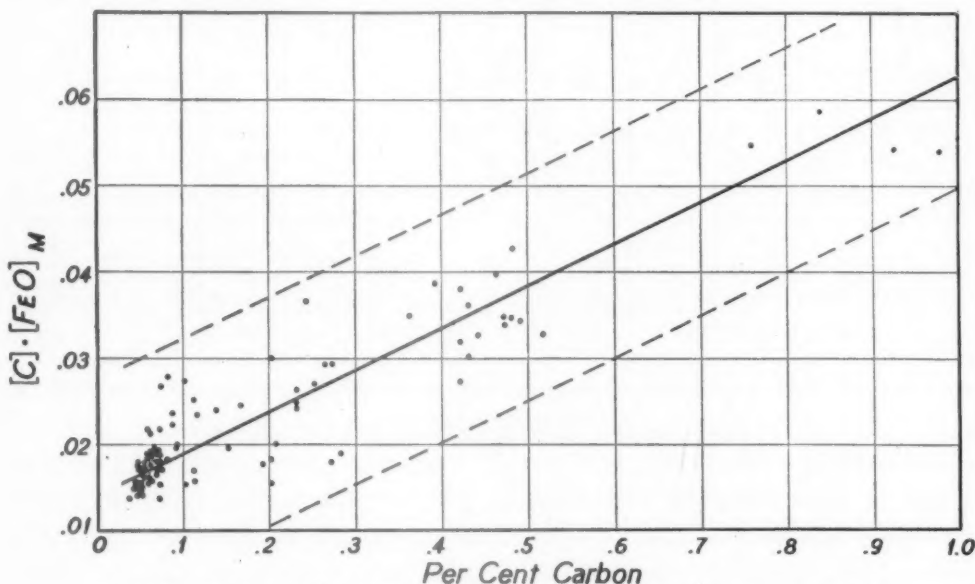


FIG. 18.—VARIATION OF  $[\text{C}] \cdot [\text{FeO}]_M$  PRODUCT WITH CARBON, PLANT A. Scatter diagram and line of regression.  $2\sigma$  limits shown.

of carbon. This is shown in Fig. 18, in which the line of regression is practically identical with the average line of Fig. 5 based upon the data of all eight cooperators. Fig. 18 illustrates beautifully the manner in which a regression line fits the data where a fairly good correlation ( $r = 0.86$ ) is obtained for a considerable number of points (122).

Fig. 19 shows the relation between the sulphur distribution ratio and basicity for each plant. Despite the fact that these lines are computed for all carbon contents for each plant, they might all be combined into a single estimate of the average sulphur-basicity relation regardless of differing bath depths, slag volumes and fuels.

As mentioned previously, the combination of the data into the eight carbon ranges and the treatment of each range as a group in Table 3 was based on the assumption that the data from all plants were representative of the same "universe." This assumption may now be further

justified on the basis of the results shown in Table 5 and in Figs. 17 to 19. Moreover, it can be shown that many of the variables within a given carbon group are independent of the source of data. Fig. 14 is a good example of this, for there the data of several plants were equally well fitted by the curved line. The authors realize that many of the variables of steelmaking are very different from one plant to another, but the interrelationships considered here appear to be very much the same from

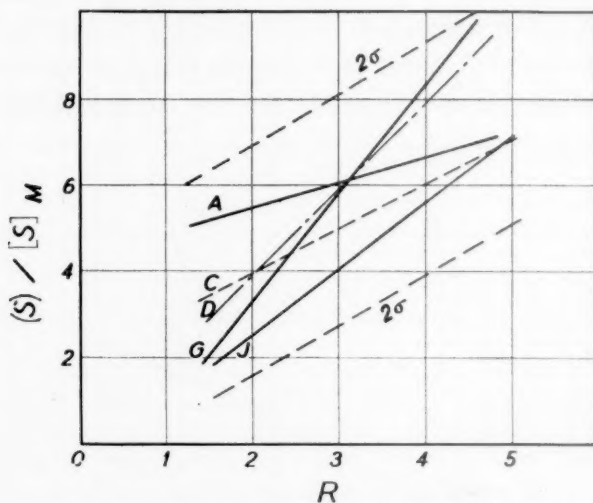


FIG. 19.—RELATION OF SULPHUR DISTRIBUTION RATIO  $(S)/[S]_M$  TO BASICITY BY PLANTS, ALL CARBON RANGES.  
Limits shown are  $2\sigma$  limits based on all data.

plant to plant despite variations in furnace dimensions, slag volumes, fuels and practices.

#### ESTIMATION OF THE IRON OXIDE CONTENT OF THE METAL

It has been shown that the oxygen content of the metal, represented by the quantity  $[\text{FeO}]_M$ , is very closely related to its carbon content. In fact, these two variables provide the highest correlation coefficients encountered in this study and the relationship is closely similar from one plant to another. Other correlations involving  $[\text{FeO}]_M$  show very much lower coefficients, which, however, are substantially improved by employing certain ratios involving  $[\text{FeO}]_M$  rather than the term itself. Thus, the distribution ratio  $(\text{FeO})_{\text{Total}}/[\text{FeO}]_M$ , at constant carbon, is related to the basicity ratio, to  $(\text{Fe}_2\text{O}_3)$ , and to  $[\text{Mn}]$ , respectively, in order of decreasing coefficients. These correlations suggest the possibility of working out a method for predicting the iron oxide content of the metal at the time the heat is ready for deoxidation without resorting to its actual determination.

The simplest and most direct means for doing this is by calculation from an accurate determination of the carbon content. It was shown

in Figs. 5 and 18 that the product  $[C] \times [FeO]_M$  is approximately a linear function of the carbon content. In order to establish this relationship a line of best fit was computed for all points, excluding approximately half of the samples from plant C, which apparently were affected by spiegel reboil.

The result of this calculation is given by the expression:

$$[C] \times [FeO]_M = 0.0124 + 0.050[C] \quad [1]$$

This equation is shown graphically in the curve of Fig. 1; it falls between the two lines of Figs. 5 and 18. Values of the average iron oxide content at round percentages of carbon are listed in Table 6.

TABLE 6.—Average Iron Oxide in Metal as a Function of Carbon Only

C.....	0.030	0.035	0.040	0.045	0.050	0.055	0.060	0.07	0.08	0.09	0.10	0.12
[FeO] <sub>M</sub> ...	0.453	0.404	0.360	0.325	0.298	0.275	0.263	0.227	0.205	0.188	0.174	0.153
[O] <sub>M</sub> .....	0.100	0.090	0.080	0.072	0.066	0.061	0.058	0.050	0.046	0.042	0.039	0.034

C.....	0.14	0.16	0.18	0.20	0.25	0.30	0.35	0.40	0.50	0.60	0.70	0.80
[FeO] <sub>M</sub> ...	0.139	0.128	0.119	0.112	0.100	0.091	0.085	0.081	0.075	0.071	0.068	0.066
[O] <sub>M</sub> .....	0.031	0.028	0.026	0.025	0.022	0.020	0.019	0.018	0.017	0.016	0.015	0.014

The standard deviation in  $[FeO]_M$  throughout this table is approximately 19 per cent of the average. An estimate of the iron oxide content of the bath based upon this table may therefore be expected to agree with that determined by the covered mold within a tolerance of 19 per cent for approximately two-thirds of the tests, or within 38 per cent in 95 out of every hundred samples. The accuracy of the estimate can be improved slightly by adjusting the constant of equation 1 according to the plant in which the sample is taken. For example, in plants A and B the best value of this constant is 0.014, and in plants G and J, 0.010, assuming the slope to be the same in all cases, which is approximately true. It is impossible to judge from the data at hand whether this represents a small actual difference in the average oxide content of the metal in the several plants or is merely the result of slight variation in methods of analysis.

A second method for estimating the degree of oxidation of the metal, and one that has been widely used, is based upon the total iron oxide content of the slag. In Table 2 the ratio  $(FeO)_{Total}/[FeO]_M$  is independent of carbon within the first five carbon groups. The average value of this ratio is 107 and accordingly the iron oxide in the metal may be estimated as  $(FeO)_{Total}/107$ . The standard deviation is 26 per cent and the estimate must be strictly confined to heats under 0.12 per cent carbon.



A similar estimate based upon the ferrous oxide of the slag is  $(\text{FeO})/77$ . This must be restricted to the same carbon range and the standard deviation is about 28 per cent.

A third independent estimate of the FeO in the steel may be made by use of the third manganese constant, which appears to be independent of carbon except in the highest carbon group. Analyses for the percentage of manganese in the slag and in the metal may be made quickly and the FeO in the metal estimated from the average value of  $K_{\text{Mn}}(3)$ , which is 252. The value of  $[\text{FeO}]_M$  estimated by this method is therefore  $252(\text{MnO})/[\text{Mn}]$  with a standard deviation of about 31 per cent. The estimate is restricted to heats under 0.31 per cent carbon.

We have made an attempt to improve upon the accuracy of these estimates by taking into account simultaneously several of the variables related to  $[\text{FeO}]_M$ . For this purpose equation 1 may be rewritten

$$[\text{C}] \times [\text{FeO}]_M = A + 0.050[\text{C}].$$

The value of the constant  $A$  for any individual test is a measure of the difference between the actual FeO in the metal and that calculated from the carbon. Values greater than the general average of 0.0124

TABLE 7.—*Correlations between Various Factors and Deviation of FeO in Metal from Its Calculated Value Based on Carbon*

$$[\text{FeO}]_M \text{ deviation} = [\text{C}] \times [\text{FeO}]_M - 0.05\text{C}$$

Variables		Number of Tests	$r$
$Y$	$X$		
$[\text{FeO}]_M$ deviation.....	$R$	376	+0.11
$[\text{FeO}]_M$ deviation.....	$(\text{FeO})_{\text{Total}}$	376	+0.14
$[\text{FeO}]_M$ deviation.....	$\text{Fe}_2\text{O}_3$	376	+0.10
$[\text{FeO}]_M$ deviation.....	$K_{\text{Mn}}(2)$	349	+0.05

represent FeO contents greater than calculated, those less represent lower oxidation than calculated from the carbon. An attempt has been made to correlate this deviation with various factors likely to be of influence. The results are shown in Table 7. As would be expected, positive correlations are observed between the  $[\text{FeO}]_M$  deviation, the slag basicity, and the slag oxidation. Although the values of the coefficients are low, the number of tests is large and the probability that the correlations are due to chance is less than 5 out of 100, except in the case of the Mn constant. The first three correlations may therefore be considered significant. On account of the wide scatter occurring with low correlation coefficients it does not appear desirable to set up a table of corrections of the calculated  $[\text{FeO}]_M$  based on these data, especially

since the method to be described in the next paragraph affords a more accurate basis of estimate.

The utilization of the methods of partial correlation and partial regression makes this fourth method of estimation possible. In any system containing three related variables it is possible to estimate the correlation between any two when the third is held constant without the necessity of subclassifying and thus greatly diminishing the data available for study. The coefficients so obtained are referred to as partial correlation coefficients and may be used to calculate regression equations expressing the values of one variable in terms of the other two. These methods are adequately described by H. T. Davis and W. F. C. Nelson<sup>7</sup> and are too detailed to be described herein.

Partial regression equations have been calculated for the FeO in the metal in terms of the carbon and the total (FeO) in the slag for various ranges of basicity. The expression is of the form:

$$[\text{FeO}]_M = \frac{f}{[\text{C}]} + g(\text{FeO})_{\text{Total}} + h \quad [2]$$

The constants  $f$ ,  $g$  and  $h$  for the various basicity groups are listed in Table 8 and may be used to estimate the FeO in the metal. Any attempt

TABLE 8.—*Calculated Values of Constants for Estimation of FeO in Metal from Carbon and Total Slag FeO*  
May be Used for Carbon Range 0.02 to 0.31 per cent

$$[\text{FeO}]_M = \frac{f}{[\text{C}]} + g(\text{FeO})_{\text{Total}} + h$$

$R$	$f$	$g$	$h$	Number of Tests
1.50-1.99	0.01360	0.00349	-0.014	15
2.00-2.24	0.01090	0.00397	-0.003	40
2.25-2.49	0.00719	0.00576	+0.002	61
2.50-2.99	0.00236	0.00847	-0.011	120
3.00-3.59	0.00540	0.00691	-0.029	74
3.60-4.09	0.00769	0.00470	-0.022	37

to read a physical significance into the apparent variation of the constants with basicity should immediately be discouraged because with the relatively limited data available it was not possible to select sufficiently large constant-basicity groups that would have random carbon distributions. The equation and its constants should then be considered merely as the best mathematically determined estimate of the FeO in the metal from the data at hand. The standard deviation of the FeO in the metal estimated by substitution of the values of Table 8 in equation 2 is about 15 per cent. This represents an improvement in estimation

over that which may be obtained from the carbon alone, or any other single factor.

While the operation of the open-hearth furnace lies beyond the scope of the present paper, it seems pertinent to inject a few words of caution regarding the uses of equation 2 either as a basis for slag control or for deoxidation. In the first place, the equation is based upon data that are not only limited in amount but which are very un-uniformly distributed as to carbon range and basicity, as may be clearly seen by inspection of Tables 1 and 8. The rounding out of the tables by supplementary data might readily make drastic changes in the terms of Table 8, with corresponding—though much smaller—changes in the calculated values of  $[\text{FeO}]_M$ . The actual effects of variations in basicity or in iron oxide of the slag cannot in any sense be judged from the terms of Table 8. Before any such physical significance could be attached to calculations like those just made it would be necessary to have as a starting point data on a large number of heats randomly distributed over the range of carbon,  $[\text{FeO}]_M$  and basicity under consideration. Obviously, with all open-hearth shops under chemical control, and with heats made under standardized practices, such a random distribution is impossible.

In the second place, the research metallurgist will not be content with an equation that is applicable only in the later stages of the heat and even then permits a deviation up to 15 per cent in about two-thirds of the tests. It is true that the equation is equally applicable in all the plants represented, and that it permits a fairly dependable estimate of a quantity that, until very recent years, was shrouded in mystery. Nevertheless, it should be possible within a given plant, and considering each grade separately, to devise a basis for estimating the degree of oxidation which will be very much more accurate. This should be especially true when methods for measuring bath temperature are available. Further, it should be pointed out that the development of greater speed in the method for determining the oxygen content of the metal will make an indirect method entirely superfluous.

Finally, it is emphasized that the calculation does not pretend to yield an absolute value for the iron oxide content of the metal. It can only give a result that is equal to that which would be determined at a certain stage of the heat by the so-called "bomb test" of McCutcheon and Rautio. Now, in spite of the fact that this method has been shown to be highly reproducible, there is no conclusive evidence that its result is the true iron oxide content of the metal. Any errors inherent in this method are, of course, implicit in all of the proposed methods of calculation. This question would be greatly clarified by an experimental comparison of the method with results obtained in the evacuated mold described by Leiber<sup>8</sup> and by Kalling and Rudberg.<sup>9</sup> Also, while there is

good precedent for calculating the oxygen of the metal to FeO, the possibility of its including other oxides would justify a preference for expressing the results simply as oxygen. For this purpose our values of  $[\text{FeO}]_M$  may be converted to  $[\text{O}]$  by dividing by 4.49.

### SUMMARY

This paper presents the results of a statistical analysis of the relationships existing between slag and metal in the basic open-hearth furnace near the end of the heat. The study was confined to tests taken on an open bath prior to addition of deoxidizers but not immediately after ore or other additions. Metal samples were obtained in the closed "bomb" type of mold, which affords the most consistent method in general use for the determination of its oxygen content. Data on 424 heats were contributed by eight steel-producing companies, comprising a total of 650 metal samples, most of which were accompanied by simultaneous slag samples.

Because of the large effect of carbon upon many of the other variables, the data were broken down into eight groups of nearly constant carbon content, as shown in Table 1. The following increase with carbon:  $[\text{C}] \cdot [\text{FeO}]_M$ ;  $[\text{Mn}]$ ;  $(\text{FeO})/[\text{FeO}]_M$ ;  $(\text{FeO})_{\text{Total}}/[\text{FeO}]_M$ ;  $(\text{S})/[\text{S}]_M$  (the last at higher carbons only). The following decrease with increasing carbon:  $[\text{FeO}]_M$ ;  $(\text{FeO})$ ;  $(\text{Fe}_2\text{O}_3)$ . The ratios  $(\text{Fe}_2\text{O}_3)/(\text{FeO})$  and  $(\text{MnO})/[\text{Mn}] \cdot (\text{FeO})$  are substantially independent of carbon content.

Within constant-carbon groups a number of relationships were found, of which the more prominent are the following: An increase in basicity is accompanied by increase in  $(\text{FeO})$ ,  $(\text{Fe}_2\text{O}_3)$ ,  $(\text{Fe}_2\text{O}_3)/(\text{FeO})$ ,  $(\text{FeO})/[\text{FeO}]_M$ ,  $(\text{FeO})_{\text{Total}}/[\text{FeO}]_M$  and  $(\text{S})/[\text{S}]_M$ . It is also attended by a decrease in the "manganese constants"  $K_{\text{Mn}}(1)$  and  $K_{\text{Mn}}(2)$ .

Within these same carbon groups it was found that there is no significant relationship between residual manganese and the iron oxide content of the metal. Further, there was no consistent relation between  $[\text{Mn}]$  and the distribution ratio  $(\text{FeO})/[\text{FeO}]_M$ , although increased residual Mn was accompanied by decrease in the ratio  $(\text{FeO})_{\text{Total}}/[\text{FeO}]_M$ .

To study the desulphurization ratio, four constant-basicity groups of low-carbon heats were selected. Within these the ratio  $(\text{S})/[\text{S}]_M$  increases with increased residual manganese, and to a lesser degree with an increase in  $K_{\text{Mn}}(2)$ .

A study of certain relationships by plants is reported in Table 5 and it is shown that the relationships studied are virtually the same from plant to plant.

Four methods are suggested for predicting the iron oxide content of the metal from other quantities that are more quickly determined by preliminary analyses. It may be estimated within a standard devia-



tion of 19 per cent from the carbon content alone (Table 6) or by considering also basicity and iron oxide in the slag, within 15 per cent (Table 8).

A complete tabulation of all of the original data used in this study is to be issued through Auxiliary Publication, and may be obtained from American Documentation Institute, 2101 Constitution Avenue, Washington, D. C., by ordering Document 1322, remitting 66¢ for copy in microfilm (read enlarged to full size on reading machines now widely available) or \$4.60 for copy in paper photoprints legible without mechanical aid.

#### ACKNOWLEDGMENTS

The authors wish to express their thanks to the representatives of the eight cooperating companies that furnished data for this study. Several of the contributors have requested that the source of their data be held confidential and for this reason the cooperators are identified only by code letters.

The analysis of the data has been accomplished with the aid of the statistical machines of the Analysis Center of the Massachusetts Institute of Technology, for the use of which and for his helpful interest the authors thank Prof. S. H. Caldwell.

Further, the authors wish to thank Prof. G. P. Wadsworth, of the Department of Mathematics of the Massachusetts Institute of Technology, for his helpful comments and criticism of the statistical methods used.

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## DISCUSSION

(Harold K. Work presiding)

L. S. DARKEN,\* Kearny, N. J.—This paper extends the use of the statistical method to steelmaking problems that are fundamental and at the same time but little understood. Feters and Chipman show clearly the value of the method for such problems by showing many statistical relationships that previously were speculative or even unsuspected. As they point out, the interpretation of the statistical results requires a high degree of metallurgical ability. It is too easy to misinterpret high correlation as causal relationship. The authors have justifiably though unfortunately omitted interpretation from this paper, since this would require a book on open-hearth practice.

Figs. 15, 16 and 19 exhibit discrepancies in the relation of the sulphur distribution to basicity and manganese between various carbon groups and various plants. This discrepancy might perhaps be minimized by considering simultaneously the slag FeO, which has been shown elsewhere to have direct bearing on the sulphur distribution. From the work of Bardenhauer and Geller, it appears that the primary composition variables determining the sulphur distribution are the "free" lime, the slag FeO, and the manganese. The (isothermal) relation is of the type  $(S)/(S)_m = A + B \left( \frac{\text{CaO}}{\text{FeO}} \right) + C[\text{Mn}]$ . Hence, it appears likely that the correlation of the sulphur distribution ratio with a ratio of "free" lime to slag FeO would be better than the corresponding correlation with basicity (or other estimate similar to "free" lime) alone.

F. G. NORRIS,† Steubenville, Ohio.—This paper is a good example of the information that can result from a systematic study of data accumulated by several plants. There are advantages in knowing whether the relations in one's own plant are normal or abnormal compared with other plants. This comparison is well made by the procedure adopted in this investigation.

The equation of the average line of Fig. 4 is:

$$\frac{\text{FeO}_T}{\text{FeO}_M} = 277C + 90$$

Combining this with equation 1 indicates that the  $\text{FeO}_T$  times C is a quadratic function of the carbon:  $13.8C^2 + 7.93C + 1.11$ . Is this conclusion true?

Was it possible from the data to study the effect of carbon drop? One of the first indirect methods for estimation of oxygen in the bath was based on carbon drop.

For any one grade (final carbon specification), the oxygen, carbon and carbon drop in the metal and the FeO and basicity of the slag will all change with the progress of the heat in such a way as to suggest conclusions that may hold only for special conditions. The 0.50 carbon point on a low-carbon heat is pretty much related to low-temperature, high-carbon drop, low basicity, low  $\text{FeO}_T$  and a high value for  $\text{FeO}_T/\text{FeO}_M$ . These conditions could all be pretty much described in terms of carbon content and might lead to a better correlation based on carbon content than is furnished by the data of the present report, which are for samples near the end of the heat.

We have obtained values for the distribution between slag and metal that are in close agreement with the equation of Fig. 4. This agreement (shown in Table 9) extends over the range 0.08 to 0.80 per cent C. The standard deviation of values calculated from the FeO and C compared with actual analysis is 0.0025 per cent oxygen. All heats were finished below 0.10C, so that the high-carbon values are early

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in the heat. Can this agreement be interpreted as indicating the importance of carbon in determining the slag-metal distribution?

What factors are in common for plants J, G and M that might explain their being close to one another but lower than the other plants?

TABLE 9.—*Variation of Oxygen Distribution with Carbon Ratio O/FeO<sub>T</sub>*

C, Per Cent	Average Value from Low-carbon Heats	Average Value from Fig. 4 (Samples near Tap)
0.80	0.00076	0.000716
0.60	0.00096	0.000872
0.50	0.00104	0.000977
0.40	0.00111	0.00111
0.30	0.00121	0.00129
0.20	0.00145	0.00153
0.10	0.00186	0.00190
0.08	0.00210	0.00199

C. B. POST,\* Reading, Pa.—The authors and the cooperating plants involved in this research are to be congratulated on the complete compilation of slag and metal samples shown in this paper and the auxiliary publication mentioned on page 198.

For some time students of melting and steel-refining problems have felt the need for representative American slag-metal basic open-hearth analyses, and these data fill a definite need in this respect.

However, the statistical analysis of such data from such diverse sources, and with complete disregard for physical properties of the slags, is open to question. This applies to the relationships involving both slag and metal samples, and not to the relationships involving the metal phase alone. The following remarks are made in a constructive spirit, and not with any idea of unfriendly criticism.

As the authors clearly state in their introductory remarks: "No attempt is made to draw comparisons between data from the two sources (laboratory and plant data), nor is an attempt made to draw conclusions as to the approach to chemical equilibrium in the open-hearth furnace." And in line with this statement, the authors have taken data from a variety of sources with a range of physical conditions, and have attempted to draw quantitative conclusions concerning the balance that exists between slags and metals in the open-hearth furnace.

Data of this sort must be either representative of equilibrium conditions or not representative. In the case at hand, both types of data are available, and the statistical analysis employed did not differentiate between the two types. This probably accounts for the large variation, sigma values, found in most of the plots.

Representative equilibrium data should be applicable to all plants and processes of steel refining. On the other hand, the slag-metal data, which represent nonequilibrium values, are of no technical use except to the plant that obtained the data. The variables affecting the approach to equilibrium must be known or controlled to enable the individual plant to use these data, unless they were taken merely for the purpose of records, and not aimed at developing methods for the control of some particular variable in the later stages of the heat.

In general, to a casual observer, the open-hearth melting and refining processes employed by industry seem to be fairly standardized, but it is well known that certain practices are employed in any given melting shop which often are applicable only in

\* The Carpenter Steel Co.

that particular plant. These may arise through the influence of the management, or the melters themselves, but the physical conditions (particularly of the slag, operating characteristics of the furnaces, etc.) generally are sufficient to differentiate one plant from another.

There is a need for some technical yardstick by which slag-metal data may be judged to be of the equilibrium or nonequilibrium type. The writer has done some research in which the heterogeneous equilibria between basic and acid slags and liquid steel are evaluated principally in terms of the "manganese" reaction. Without going into details, it is thought the equilibrium "manganese" content of a bath may be judged from the slag analysis. Fig. 20 shows some of the data considered by the authors from plants B, C, D and G. The graphical appearance of these data leads to the belief that the method proposed does distinguish between equilibrium and non-equilibrium conditions, otherwise the average slope of the line would not be unity.

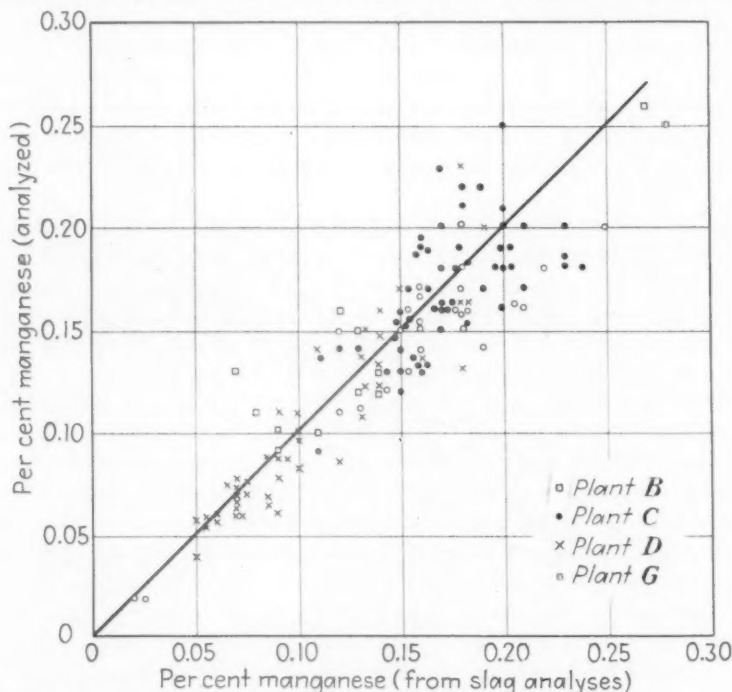


FIG. 20.—COMPARISON OF EXPERIMENTAL MANGANESE CONTENT OF BASIC OPEN-HEARTH STEEL WITH EQUILIBRIUM MANGANESE CONTENT FROM SLAG ANALYSIS.

Fig. 21 shows the determined FeO in the slag versus the percentage of FeO in the metal for some of the data from plants A, B, C, D and G. The points enclosed by circles represent the slags that are at equilibrium with the bath, judged by the "manganese" reaction. Fig. 21 shows clearly that the spread of the variation is considerably reduced when the data are treated in this manner, and furthermore, no significant variation exists from one plant to another.

The question of equilibrium between slag and metal should not enter into the relationships found by Feters and Chipman when the metal phase alone is considered. The variation of  $C \times \text{FeO}$  product with carbon, while perhaps representing operating conditions in the open hearth, certainly cannot be considered to represent the equilibrium value of this product. The authors themselves would probably concur in this belief.

In basic electric-arc furnace practice the evaluation of this product can be obtained when the rate of reaction of carbon with ferrous oxide is zero. The accompanying

data of The Carpenter Steel Co. compared with the data of Chipman and Fetters are significant and pertinent in this respect. The ferrous oxide contents were determined by means of aluminum-killed samples using aurintricarboxylic acid as a colorimetric agent for the determination of alumina.

C, Per Cent	C $\times$ FeO	
	Chipman and Fetters	Carpenter Steel Co.
0.10	$0.019 \pm 0.01$	0.010-0.015
0.50	$0.038 \pm 0.01$	0.015-0.020
1.00	$0.062 \pm 0.01$	0.025-0.030

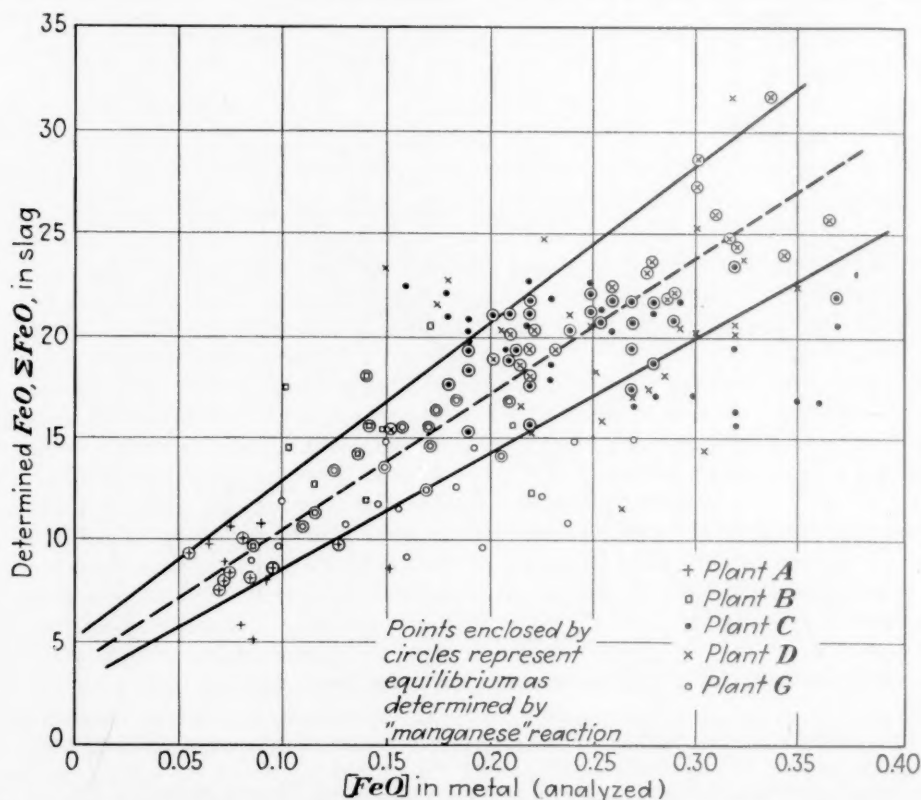


FIG. 21.—DETERMINED FeO IN SLAG VERSUS PERCENTAGE OF FeO IN METAL FOR SOME DATA FROM VARIOUS PLANTS.

K. L. FETTERS AND J. CHIPMAN (authors' reply).—While we thought it necessary to omit detailed interpretations from the paper, we hoped that many such points as Dr. Darken mentions would be raised in discussion. The relationship he mentions could be investigated by the method of partial correlation, and the results would be of considerable interest. The effect of FeO is shown indirectly in the observed effect of carbon, but a more direct treatment would be desirable.

In order to answer Mr. Norris' first question, it is necessary that certain characteristics of a line of regression be thoroughly understood. That the relationship between two variables can be expressed by such a line does not imply that this relationship is strictly linear. The regression line is simply the best straight line that can be drawn through the average values of  $Y$  at each value of  $X$ . Two such lines cannot be



combined to determine the *form* of the third relationship. In the present instance, therefore, we should not be justified in concluding that a quadratic relationship exists, but merely that *if* the relationship is quadratic the equation will represent the average value of  $[C] \times (\text{FeO})_{\text{Total}}$  at any value of  $[C]$ . Actually it does this quite well in the range included in Fig. 4, as can easily be verified by solving Mr. Norris' equation and comparing with the upper line of Fig. 2.

Data on rate of carbon drop were not submitted by enough plants to warrant the inclusion of this variable in the study. This rate, and indeed the entire problem of open-hearth kinetics, affords a fertile and important field for further investigation.

Mr. Norris' report that the distribution ratio is the same function of carbon early in the heat as we have found under finishing conditions is indeed interesting. Not only does this emphasize the importance of carbon but it also indicates a close control of slag basicity in the practice employed. This effect of carbon is interpreted as evidence that the carbon-oxygen reaction in the metal is more rapid than the diffusion of iron oxide from slag to metal. The higher carbon heats are thus farther removed from distributional equilibrium than those at lower carbon.

As far as we are aware, there are no factors common to plants J, G and M that are not also common to the other plants. The slight characteristic difference noted may have been due to differences in sampling and analytical techniques as well as to operating methods.

Dr. Post need make no apology for his interesting contributions. We agree that the data would have been more complete if the physical nature of the slag could have been included. It would have been instructive to have also the mineralogical constituents of the slag, the rate of carbon drop and the temperature of the bath.

Dr. Post's remarks as to the justification of the use of statistical methods without due regard for the physical condition of the slag bring out one of the chief advantages of statistical methods; namely, that by the use of a large number of tests the condition of the individual test is of little concern and does not seriously detract from the utility of the relationship observed. It is desirable, where sufficient information is available, to subclassify a set of data into metallurgical logical subgroups (as was done with respect to carbon in the present paper) but a statistical analysis of value may be made where such factors are unknown or unsuspected providing that a *sufficiently large* number of tests are available. It is appreciated that the scatter and the resulting standard deviation or sigma values will be higher where such general considerations must be applied. Fig. 10, which shows the variation of the  $(\text{Fe}_2\text{O}_3):(\text{FeO})$  ratio with basicity  $R$  is an example of data that have been used without restriction. The scatter is wide but the trend is certain that at higher basicity values the  $(\text{Fe}_2\text{O}_3):(\text{FeO})$  ratio is likely to be higher whether due to chemical or physical condition of the slag or to a combination of the two. Statistical methods do not and cannot be expected to answer the question "Why?"

Restriction of slag-metal data by elimination of the tests that do not satisfy the manganese equilibrium no doubt seems to reduce the variation in the  $[\text{FeO}] - (\text{FeO})_{\text{Total}}$  relation, as indicated in Fig. 21. Whether this restriction has eliminated the non-equilibrium data or only the tests that represented "end items" of the temperature or basicity distributions, is open to question. The authors prefer to await the experimental determination of what constitutes equilibrium between slag and metal before attempting to apply the equilibrium concept too enthusiastically to the basic open-hearth process.

Finally, the authors wish to express their surprise that no one has raised a question regarding phosphorus. The behavior of this element has given us no little concern and the data as yet have yielded practically no reasonable conclusions. We plan to devote further study to this question and hope to make it the subject of a future communication.



## Equilibria in Liquid Iron with Carbon and Silicon

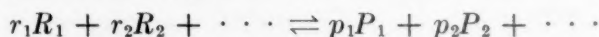
By L. S. DARKEN\*

(New York Meeting, February 1940)

In the study of reactions occurring in liquid iron, alone or in contact with a liquid oxide or slag phase, it has been found that the experimental data over a limited range of concentration can in some cases be represented satisfactorily by the simple equilibrium expression

$$K = \frac{(P_1)^{p_1}(P_2)^{p_2} \cdots}{(R_1)^{r_1}(R_2)^{r_2} \cdots}$$

where (*P*) denotes the concentration of a product and (*R*) the concentration of a reactant in the reaction



Some of the reactions for which it holds are listed in Table 1. For others, however, the simple equation apparently does not hold. This has been attributed to an improper method of expressing concentration (for instance, weight per cent instead of mol fraction); or it has been supposed that the solutions are not ideal in the sense that the activity of a component is not proportional to its true mol fraction. But it may be that the problem has been oversimplified by neglecting some molecular species actually present; that is, by considering only the ostensible simple components and thus leaving out of account possible compound formation. It is the purpose of the present paper to point out how, in a group of related cases, a reasonable consistent assumption relative to the presence of a compound makes it possible to express the experimental data satisfactorily by the simple equilibrium expression when this compound is taken into account, and to bring into harmony data referring to different reactions in liquid iron.

There are several *a priori* reasons for believing that solutions in liquid iron should not deviate far from ideality, provided that the concentration of solute is not too great and is expressed in proper terms. The factors that commonly lead to nonideality in systems at ordinary temperature—as ionization or the occurrence of polar and nonpolar molecules—are presumably less effective in metal and in slag systems at high temperature. Again, the type of equation commonly used to express the value of

Manuscript received at the office of the Institute Nov. 28, 1939. Issued as T.P. 1163 in METALS TECHNOLOGY, February 1940.

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activity coefficients shows that there exists an inverse relationship between the logarithm of this coefficient and the absolute temperature, whence it follows that, other things being equal, the activity coefficient is more nearly unity at high values of  $T$ . This may be stated in another way: at high temperatures molecules are less influenced by their neighbors, or thermal energy becomes a dominant factor in the result. In general, any compounds present in appreciable concentration at high temperature are few in number and stoichiometrically simple. This general line of reasoning led to an attempt to account for the apparent deviation from ideality in the liquid systems Fe-C and Fe-C-Si on the basis that a compound is in fact present. These systems were chosen because the avail-

TABLE 1.—Some Investigated Equilibria of Interest in Steelmaking

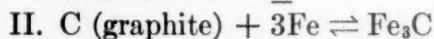
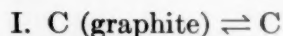
Reaction <sup>a</sup>	Equilibrium Constant Essentially as Expressed by Investigator	Reference
$\text{FeO} \rightleftharpoons \underline{\text{FeO}}$ .....	$\frac{[\text{FeO}^*]}{(\text{FeO}^*)}$	C. H. Herty, Jr.: <i>Carnegie Inst. Tech. Bull.</i> 34 (1927). F. Körber: <i>Stahl und Eisen</i> (1932) <b>52</b> , 133.
$\text{MnO} + \underline{\text{Fe}} \rightleftharpoons \text{FeO} + \underline{\text{Mn}}$ .....	$\frac{[\text{Mn}^*](\text{FeO}^*)}{(\text{MnO}^*)}$	F. Körber: <i>Stahl und Eisen</i> (1932) <b>52</b> , 133.
$\text{FeS} \rightleftharpoons \underline{\text{FeS}}$ .....	$\frac{[\text{S}^*]}{(\text{S}^*)}$	P. Bardenheuer and W. Geller: <i>Mitt. K.W.I. Eisenforschung</i> , Düsseldorf (1934) <b>16</b> , 77. Meyer and Schulte: <i>Archiv Eisenhüttenwesen</i> (1934) <b>8</b> , 187.
$\underline{\text{Fe}} + \text{H}_2\text{S} \rightleftharpoons \text{H}_2 + \underline{\text{FeS}}$ .....	$\frac{[\text{S}^*] p_{\text{H}_2}}{p_{\text{H}_2\text{S}}}$	J. Chipman and Ta Li: <i>Trans. Amer. Soc. Metals</i> (1937) <b>25</b> , 435.
$\underline{\text{FeS}} + \text{CaO} \rightleftharpoons \text{CaS} + \underline{\text{FeO}}$ ....	$\frac{(\text{S}^*)(\text{FeO}^*)}{[\text{S}^*](\text{CaO}^*)}$	P. Bardenheuer, and W. Geller: <i>Mitt. K.W.I. Eisenforschung</i> , Düsseldorf (1934) <b>16</b> , 77.
$\underline{\text{Mn}} + \text{FeS} \rightleftharpoons \text{MnS} + \underline{\text{Fe}}$ .....	$\frac{(\text{MnS})[\text{Fe}]}{(\text{FeS})[\text{Mn}^*]}$	Meyer and Schulte: <i>Archiv Eisenhüttenwesen</i> (1934) <b>8</b> , 187.
$\text{Si} + 2\underline{\text{FeO}} \rightleftharpoons \underline{\text{Fe}} + \text{SiO}_2$ .....	$\frac{1}{[\text{Si}^*][\text{FeO}^*]}$	P. Bardenheuer and W. Geller: <i>Mitt. K.W.I. Eisenforschung</i> , Düsseldorf (1934) <b>16</b> , 77.
$\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$ .....	$\frac{p_{\text{CO}}^2}{p_{\text{CO}_2}[\text{C}^*]}$	F. Körber and W. Oelsen: <i>Mitt. K.W.I. Eisenforschung</i> , Düsseldorf (1933) <b>15</b> , 271; (1936) <b>18</b> , 109.
$\underline{\text{Fe}} + \text{CO}_2 \rightleftharpoons \underline{\text{FeO}} + \text{CO}$ .....	$\frac{[\text{FeO}^*] p_{\text{CO}}}{[\text{C}^*][\text{O}^*]}$	H. C. Vacher and E. H. Hamilton: <i>Trans. A.I.M.E.</i> (1931) <b>95</b> , 124.
$\text{C} + \underline{\text{FeO}} \rightleftharpoons \text{CO} + \underline{\text{Fe}}$ .....	$\frac{1}{[\text{C}^*][\text{O}^*]}$	H. C. Vacher: <i>Nat. Bur. Stds. Jnl. of Research</i> (1933) <b>11</b> , 541.
$\underline{\text{FeO}} + \text{H}_2 \rightleftharpoons \underline{\text{Fe}} + \text{H}_2\text{O}$ .....	$\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}[\text{FeO}^*]}$	J. Chipman and A. M. Samarin: <i>Trans. A.I.M.E.</i> (1937) <b>125</b> , 331.

<sup>a</sup> Molecular species underlined are in solution in liquid iron. A symbol in brackets denotes concentration in the metal phase; in parentheses, in the oxide or slag phase. Concentration is expressed in mols except where the symbol is starred, when it represents weight per cent.

able data seem to be reasonably good and to cover a number of aspects of the two systems; also because Oelsen<sup>1</sup> has recently shown that his experimental data on the Fe-C-Si-Mn system are not in accord with the simple interpretation of the ideal equilibrium law, and a proper interpretation is of some practical importance.

### THE LIQUID SYSTEM IRON-CARBON

In Fe-C melts the possible molecular species are Fe, C, with their possible polymers, and compounds of the type  $\text{Fe}_v\text{C}_z$ , presumably mainly  $\text{Fe}_3\text{C}$ . Chipman<sup>2</sup> has shown that the data of Ruer and Biren<sup>3</sup> on the solubility of graphite in liquid iron cannot be consistently interpreted in terms of the presence of the carbon in any *single* form. It will be shown that these data can be reproduced by collating them with data on other equilibria by formal application of the law of mass action and the simple integrated form of the van't Hoff equation, by making the assumption that the co-existing molecular species are Fe, C, and  $\text{Fe}_3\text{C}$ . On this basis the primary equilibria to be considered are:



where in such a chemical equation a symbol is underlined to denote that the molecular species is in solution; the number of mols of each species present in the total amount under consideration will be represented throughout this paper by use of a bracket about the symbol.\* If  $N$  is the total number of mols, namely  $[\text{Fe}] + [\text{Fe}_3\text{C}] + [\text{C}]$ , and the solution is regarded as ideal, then (taking the activity of graphite as unity)

$$\frac{[\text{C}]}{N} = K_1 \quad [1]$$

$$\frac{[\text{Fe}_3\text{C}]N^2}{[\text{Fe}]^3} = K_2 \quad [2]$$

From the observed total solubility of graphite in iron at any temperature (as given for a series of temperatures in column 8 of table 2), can be derived corresponding values of  $C_M$  and  $\text{Fe}_M$ , the total number of mols of carbon and of iron in the solution; these are equal respectively to  $[\text{C}] + [\text{Fe}_3\text{C}]$  and to  $[\text{Fe}] + 3[\text{Fe}_3\text{C}]$ . By substitution in equations 1 and 2 these individual concentrations can be eliminated and eq. 2a be obtained:

$$\{\dot{C}_M(1 - K_1) - \text{Fe}_M K_1\} \frac{\{\text{Fe}_M - 2C_M\}^2}{\{\text{Fe}_M - 3C_M(1 - K_1)\}^3} = K_2 \quad [2a]$$

<sup>1</sup> References are at the end of the paper.

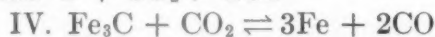
\* The concentrations in the liquid phase as used throughout this paper are not to be confused with various purported estimates based on analysis of the solid. In particular  $\text{Fe}_3\text{C}$  has no relation to the "combined carbon" as frequently used in the literature to designate the nongraphitic carbon in the cooled solid metal.

$K_2$  cannot be zero as long as  $[\text{Fe}_3\text{C}]$  is not zero; hence the left-hand side of eq. 2a cannot be zero, and it follows that at the temperature at which in the liquid  $\text{Fe}_M = 2C_M$  the quantity

$$\frac{[\text{Fe}_M - 3C_M(1 - K_1)]^3}{C_M(1 - K_1) - \text{Fe}_M K_1}$$

shall be zero and consequently  $K_1$  is then  $\frac{1}{3}$ .<sup>\*</sup> When  $\text{Fe}_M = 2C_M$  the solubility is 9.71 when expressed in terms of percentage by weight of carbon dissolved; and this value is reached, according to Ruer and Biren, at a temperature of about 2500°C.

On the basis of the existence of the molecular species  $\text{Fe}_3\text{C}$ , the value of  $K_1$  at 2500°C. is thus 0.333 from the solubility measurements. Its value at another temperature can be calculated from the measurements of the solubility of graphite and of the equilibrium between CO and  $\text{CO}_2$  in contact with (III) graphite, (IV) liquid iron containing small percentages  $[\text{C}^*]$  of carbon.<sup>†</sup> At 1580°C. for equilibrium III,  $p_{\text{CO}}^2/p_{\text{CO}_2} = 17,100$ , the mean between 15,800 as given by Chipman<sup>2</sup> and 18,400, according to Kelley and Anderson;<sup>4</sup> for IV at the same temperature, according to Vacher and Hamilton,<sup>5</sup>  $p_{\text{CO}}^2/p_{\text{CO}_2} = 378$  ( $\text{C}^*$ ). The corresponding reactions are



whence

$$\frac{p_{\text{CO}}^2}{p_{\text{CO}_2}} = K_3 \quad [3]$$

$$\frac{p_{\text{CO}}^2}{p_{\text{CO}_2}} = K_4 \frac{[\text{Fe}_3\text{C}]N^2}{[\text{Fe}]^3} \quad [4]$$

or

$$\frac{[\text{Fe}_3\text{C}]N^2}{[\text{Fe}]^3[\text{C}^*]} = \frac{378}{K_4} \quad [4a]$$

To correlate the several data, we calculate approximate limiting values for  $[\text{Fe}_3\text{C}]$ ,  $[\text{Fe}]$ ,  $N$  at zero concentration of carbon on the assumption that all carbon is then present as  $\text{Fe}_3\text{C}$ ; that is, that  $m[\text{C}^*] = [\text{Fe}_3\text{C}]$ ,  $m$  being the factor required for conversion from weight per cent to mol

<sup>\*</sup> This may be demonstrated more easily from the expression  $N = \frac{\text{Fe}_M - 2C_M}{1 - 3K_1}$ .

Now surely  $N$  cannot be zero; hence the numerator  $(\text{Fe}_M - 2C_M)$  cannot be zero unless the denominator  $(1 - 3K_1)$  be also zero. More generally if the derivation be carried through for  $\text{Fe}_n\text{C}$  instead of  $\text{Fe}_3\text{C}$  it is found that at the concentration at which  $\text{Fe}_M = (n - 1)C_M$ ,  $K_1 = 1/n$ .

<sup>†</sup> The asterisk applied to a symbol for a molecular species is used throughout this paper to indicate weight per cent; in equations in which such designation is used all other symbols must of course refer to a total mass of 100 (conveniently taken as 100 grams).



fraction at the concentration in question. On this basis\*  $K_4 = 8120$ , whence, as a first approximation  $K_2 = \frac{K_3}{K_4} = \frac{17,100}{8120} = 2.11$  at  $1580^\circ\text{C}$ .

From this value in conjunction with the solubility data,† a value for  $K_1$  may be calculated, hence a second value for  $K_4$ . By successive approximations we finally have  $K_1 = 0.067$ ,  $K_2 = 2.04$  at  $1580^\circ\text{C}$ .‡

There has now been derived a value of  $K_1$  for each of two temperatures; namely, 0.067 at  $1580^\circ$  ( $T = 1853$ ) and 0.333 at  $2500^\circ$  ( $T = 2773$ ).

Making the very reasonable assumption that  $\log K_1 = \frac{A}{T} + B$ , and substituting the pairs of values, we reach the expression

$$\log K_1 = -3890/T + 0.926$$

which permits us to calculate  $K_1$  at any temperature ( $T$  absolute) within the range, and to estimate that  $\Delta H_1$ , the heat of this reaction, is 17,800 calories.§

It remains to find  $K_2$  at some temperature other than  $1580^\circ\text{C}$ . ( $T = 1853$ ). Choose  $1150^\circ\text{C}$ . ( $T = 1423$ ), for which  $K_1$ , as calculated from the expression above, is 0.016 and  $[C^*]$  is, from the solubility measurements, 4.24; on this basis  $K_2 = 1.08$  (from eq. 2a). Combining the pairs of values as before gives

$$\log K_2 = -1710/T + 1.234$$

and accordingly  $\Delta H_2$  is about 7800 calories.

Both  $K_1$  and  $K_2$  can now be computed, and hence  $C_M$ , for each temperature, and the results can be compared with the direct experimental values of Ruer and Biren, as is done in Table 2. The agreement is quite satisfactory.

It is interesting that if the presence is assumed, not of  $\text{Fe}_3\text{C}$  as was done above, but of  $\text{Fe}_2\text{C}$  or  $\text{FeC}$ , and the same calculations are performed, the results are absurd. This is regarded as corroborative evidence that if only one carbide is present in substantial proportions, it is  $\text{Fe}_3\text{C}$ .

\* On this same basis Vacher<sup>6</sup> gives 7900 for  $K_4$  at  $1580^\circ\text{C}$ ., as the outcome of newer measurements, which agreed satisfactorily with the earlier measurements of Vacher and Hamilton.<sup>5</sup>

† The solubility of graphite in iron is here taken as 5.31 per cent in exact agreement with the measurements of Herty and Royer,<sup>7</sup> which are used later in calculations of the C-Fe-Si equilibrium. The value given by Ruer and Biren (5.36 per cent) is not significantly different; the value of  $K_1$  calculated therefrom is 0.072.

‡ If the calculations are carried out for each of the two values given above for  $K_1$ , the resulting values of  $K_2$  are 1.95 and 2.26, respectively.

§ It is interesting to note that this equation predicts the melting point of graphite as  $3928^\circ\text{C}$ . (ignoring the pressure correction); the melting point of graphite is not known with any degree of precision but this value is certainly of the right order of magnitude.



An independent check on the reasonableness of this viewpoint is afforded by a comparison with the result of Chipman's<sup>2</sup> calculation, based on Ruff and Borman's data on vapor pressures, that at 2650°C. the mol fraction of iron in iron saturated with graphite is 0.39. The value of this quantity, calculated for this temperature from the values of  $K_1$  and  $K_2$  derived from the equations given above, is 0.37, which is quite as close as could be expected in view of the uncertainties in the experimental data involved in these several calculations.\*

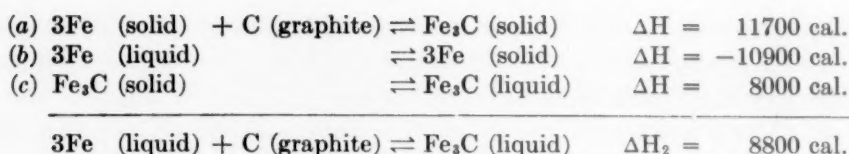
TABLE 2.—*Solubility of Carbon in Liquid Iron Saturated with Graphite*<sup>a</sup>

<i>t</i> °C.	Calculated		Mol Fractions from $K_1$ and $K_2$			Percentage Carbon by weight	
	$K_1$	$K_2$	Fe	Fe <sub>3</sub> C	C	Calculated	Observed (Ruer and Biren) from Smoothed Curve up to 1900°C.
1150	0.016	1.08	0.666	0.318	0.016	4.24	4.24
1200	0.019	1.18	0.653	0.328	0.019	4.36	4.36
1300	0.028	1.40	0.627	0.345	0.028	4.60	4.62
1400	0.041	1.63	0.603	0.356	0.041	4.86	4.88
1500	0.054	1.86	0.581	0.365	0.054	5.10	5.15
1600	0.071	2.09	0.561	0.368	0.071	5.37	5.41
1700	0.090	2.27	0.541	0.369	0.090	5.65	5.66
1800	0.112	2.56	0.523	0.365	0.112	5.96	5.96
1900	0.137	2.80	0.504	0.359	0.137	6.31	6.33
2000	0.164	3.03	0.487	0.349	0.164	6.71	6.76
2100	0.194	3.26	0.469	0.337	0.194	7.17	7.31
2200	0.226	3.49	0.452	0.322	0.226	7.68	7.77
2300	0.260	3.71	0.435	0.305	0.260	8.27	8.30
2400	0.296	3.93	0.418	0.286	0.296	8.92	8.89
2500	0.333	4.14	0.400	0.266	0.333	9.72	9.52
2600	0.374	4.35	0.382	0.244	0.374	10.71	11.15
2700	0.416	4.56	0.364	0.220	0.416	11.96	

<sup>a</sup> Ruer and Biren's results.<sup>20</sup>

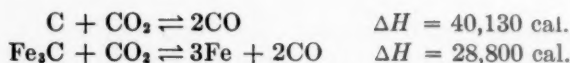
A further check on the plausibility of the equations derived to express the homogeneous equilibrium in the liquid system Fe-C is afforded by a comparison of the heat of reaction ( $\Delta H_2 = 7800$ ) derived from the rate of change of  $K_2$  with temperature with that calculated by combining independent data (in the neighborhood of the eutectic temperature), as follows:

\* Chipman's conclusion that the *average* composition of the solute (carbon) at 2650°C. is Fe<sub>3</sub>C (at saturation) is not in disagreement with the present discussion, which treats the carbon as existing as two species, namely C and Fe<sub>3</sub>C; the average composition at 2650°C. of the C and Fe<sub>3</sub>C, indeed, corresponds nearly to Fe<sub>3</sub>C.



which is as close to 7800 as is to be expected by reason of the uncertainty of the data used. The values for the three reactions were derived as follows:

(a) The value 11,700 cal. is the mean of Austin's (J. B. Austin, private communication) estimate of 12,000 cal. (based on Roth's value of 4400 at room temperature) and of the value 11,300 as calculated from the equilibrium data by: (1) Kelley and Anderson<sup>4</sup> and (2) Chipman<sup>2</sup> for the pair of reactions:



(b) The best value of the heat of fusion of iron is about 3630 cal. per mol, according to Cleaves and Thompson.<sup>8</sup>

(c) The heat of fusion of Fe<sub>3</sub>C as calculated by Umino is 11,600 cal. per mol; as derived from Umino's<sup>9</sup> mean value for the heat of the eutectic reaction it is 7900, and from the slope of his equilibrium curve it is 7800 on the basis that Fe<sub>3</sub>C remains substantially undissociated, or some 3500 cal. lower, if dissociation be taken into account. Graphitization, if it occurs, would cause a large error but the error would be in opposite direction for the two different methods of calculation. As a tentative value, we take 8000 cal. per mol as the heat of fusion of Fe<sub>3</sub>C.

Thus by combining various data relating to the liquid system Fe-C it has been possible, by assuming the presence of a compound Fe<sub>3</sub>C, to correlate them, the concordance being as good as the concordance between the same nominal data from different observers. At the least, there is a more consistent picture than existed before, and approximate calculations can be made for comparison with and interpretation of experiment.

#### THE LIQUID SYSTEM IRON-CARBON WITH A THIRD ELEMENT

When a third element *X* is added to a liquid solution of iron saturated with graphite, let it be assumed that in certain cases the main reaction is  $n\text{Fe} + \text{X} \rightleftharpoons \text{Fe}_n\text{X}$ , and that the only molecular species that need be taken into account are Fe, C, X, Fe<sub>3</sub>C and Fe<sub>*n*</sub>X. Then, in addition to eqs. 1 and 2 there is, by definition,

$$\frac{[\text{Fe}_n\text{X}]\text{N}^n}{[\text{Fe}]^n[\text{X}]} = K_5 \quad [5]$$

together with the stoichiometric conditions

$$\begin{aligned}
C_M &= [C] + [Fe_3C] \\
X_M &= [X] + [Fe_nX] \\
Fe_M &= [Fe] + n[Fe_nX] + 3[Fe_3C] \\
N &= [C] + [Fe_3C] + [X] + [Fe_nX] + [Fe] = C_M + X_M + [Fe]
\end{aligned}$$

There are thus seven equations (the five above and eqs. 1 and 2) and six quantities ( $N$  and the mols of each of the five molecular species) which are not directly measurable; it is possible therefore to eliminate these quantities and obtain a single equation in which they do not appear. This is hardly practicable, but the seven equations are readily reduced to two (in which  $N$  is the only one of the six quantities mentioned that appears), as follows:

$$\begin{aligned}
& Fe_M - 3(C_M - NK_1) - \left\{ \frac{N^2}{K_2} (C_M - NK_1) \right\}^{1/2} \\
& \left[ \frac{C_M - NK_1}{NK_2} \right]^{n/3} \left\{ nX_M - Fe_M + 3(C_M - NK_1) - \left[ \frac{N^2}{K_2} (C_M - NK_1) \right]^{1/2} \right\} \\
& \hspace{25em} = K_5 \quad [5a]
\end{aligned}$$

$$C_M + X_M + N \left[ \frac{C_M - NK_1}{K_2} \right]^{1/3} = N \quad [5b]$$

Let us first consider the special case that  $X$  forms no compound with iron. On this basis  $K_5 = 0$ , consequently the numerator of equation 5a is likewise zero. This equality can be used to calculate  $C_M$  when  $K_1$  and  $K_2$  are known. It is simplest to set  $N$  equal to 1, which merely fixes the total amount of the system under consideration; and eqs. 5a and 5b then become

$$\begin{aligned}
Fe_M &= 3C_M - 3K_1 + \left( \frac{C_M - K_1}{K_2} \right)^{1/2} \\
X_M &= 1 - C_M - \left( \frac{C_M - K_1}{K_2} \right)^{1/2} = 1 + 2C_M - 3K_1 - Fe_M
\end{aligned}$$

whence, by insertion of the values of  $K_1$  and  $K_2$  appropriate to the temperature,  $C_M$  may be calculated for any values of  $Fe_M$  and  $X_M$ , and the results compared with experimental data on the solubility of graphite in liquid iron containing  $X$ .

This comparison is made most easily if we convert from mols to weights and thence to percentage by weight and plot these percentages as a function of  $X$  in percentage by weight. This has been done on the basis that  $X$  has an atomic weight of 27 (aluminum), and the resulting curve in Fig. 1 is compared with the experimental data of Vogel and Mäder,<sup>10</sup> also with a curve derived on the basis that there is no free carbon in solution in the iron. Their data obviously are not accurate enough to make possible a decision as to which curve is the better, though the agreement with either is reasonably good. It is to be noted that in this case

the calculation does not require successive approximations or the solution of equations of higher power than the first.

For values of  $K_3$  other than zero—that is, if there is some compound of  $X$  with iron—the procedure is similar. From the relation

$$X_M = 1 - C_M - \left( \frac{C_M - K_1}{K_2} \right)^{1/3}$$

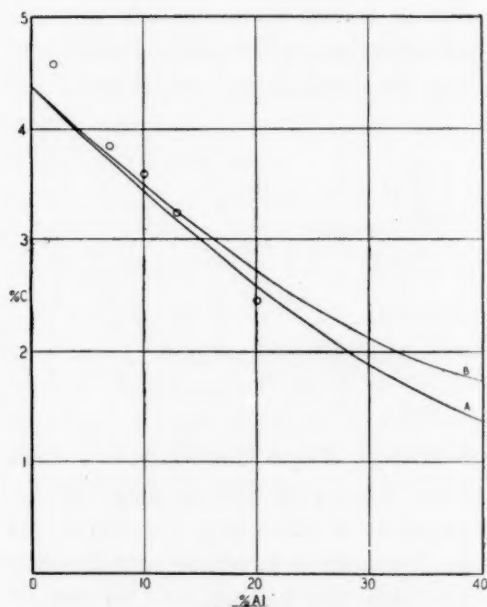


FIG. 1.

FIG. 1.—SOLUBILITY OF GRAPHITE IN IRON-ALUMINUM ALLOYS AT 1200°C.

Curve A, calculated from  $K_1 = 0.019$ ;  $K_2 = 1.18$

Curve B, calculated from  $K_1 = 0$ ;  $K_2 = 1.45$

Points are Vogel and Mäder's extrapolation of their data.

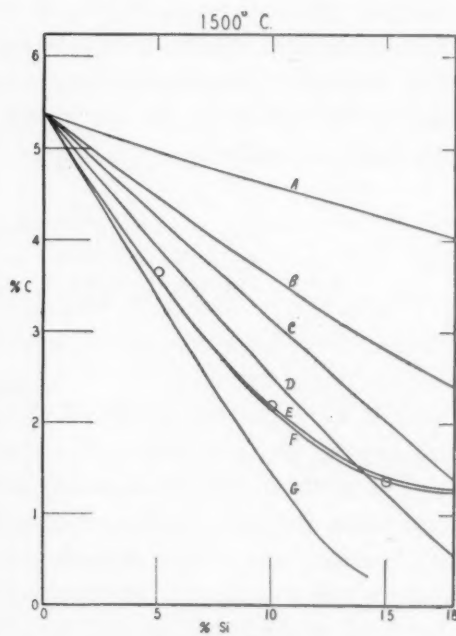


FIG. 2.

FIG. 2.—SOLUBILITY OF GRAPHITE IN IRON-SILICON MELTS AT 1500°C. CONCENTRATION EXPRESSED IN RELATION TO TOTAL IRON PLUS SILICON. COMPARISON OF EXPERIMENTAL DATA WITH VARIOUS HYPOTHESES.

Curve	Silicon Compound Considered	Value of Constant	Curve	Silicon Compound Considered	Value of Constant
A	none		E	$\text{Fe}_3\text{Si}$	45
B	$\text{FeSi}$	$\infty$	F	$\text{Fe}_2\text{Si}$	50
C	$\text{Fe}_3\text{Si}_2$	$\infty$	G	$\text{Fe}_2\text{Si}$	$\infty$
D	$\text{Fe}_2\text{Si}$	$\infty$			

corresponding values of  $X_M$  (from arbitrarily chosen values of  $C_M$ ) are obtained and inserted in eq. 5, preferably rewritten as follows:

$$\text{Fe}_M = 1 + 2C_M - X_M - 3K_1 + \frac{nX_M}{\frac{1}{K_5} \left( \frac{K_2}{C_M - K_1} \right)^{n/3} + 1}$$

By assuming pairs of values of  $K_5$  and  $n$  it is then possible to calculate the curves just as in the preceding case. A group of such curves has been calculated on the basis that  $X$  is silicon (at. wt. 28) and that  $K_5$  is (A) zero; that  $K_5$  is infinite—that is, that the silicon exists wholly as (B) compound  $\text{FeSi}$  ( $n = 1$ ), or (D)  $\text{Fe}_2\text{Si}$  ( $n = 2$ ), or (G)  $\text{Fe}_3\text{Si}$  ( $n = 3$ ); or that  $K_5$  is (E) 45 with  $n = 3$ , or (F) 50 with  $n = 3$ . These curves are reproduced in Fig. 2, with the experimental points at  $1500^\circ\text{C}$ . of Herty and Royer.<sup>7</sup> (Also included in the figure is the calculated curve (C) corresponding to the condition that all the silicon exists as the compound  $\text{Fe}_3\text{Si}_2$ .) The figure shows that the experimental points lie between the curves for  $K_5 = 0$  and  $K_5 = \infty$  only when  $n$  is 3. On this basis the reaction in liquid iron is  $3\text{Fe} + \text{Si} \rightleftharpoons \text{Fe}_3\text{Si}$ , and the best value of the quotient  $\frac{[\text{Fe}_3\text{Si}]N^3}{[\text{Fe}]^3[\text{Si}]}$  is near 45 for  $1500^\circ\text{C}$ ., as is clear from Fig. 2. (Percentage of carbon in this figure is taken as grams C per 100 grams Fe + Si.)

An identical procedure applied to the data of Herty and Royer for the other temperatures and to the data of Hanemann and Jass<sup>11</sup> for the "eutectic" composition ( $1153^\circ$  to  $1200^\circ$ ) led to the following values of  $K_5$ :

(ca. $1175^\circ$ )	$1300^\circ$	$1500^\circ$	$1600^\circ$	$1700^\circ$
$K_5 = 25 \pm 5$	$30 \pm 6$	$45 \pm 8$	$60 \pm 9$	$75 \pm 10$

all of which are reproduced satisfactorily by the equation\*

$$\log K_5 = -3150/T + 3.45$$

The constant for any temperature may also be calculated directly by substitution of the individual experimental data in eqs. 5a and 5b; but this procedure is more complex and in general is less satisfactory because the relation between a fixed experimental error and the calculated value of  $K_5$  varies markedly with concentration. For concentrations of silicon less than 15 per cent, the values of this constant are essentially unaffected, within the experimental error, by the assumption that no free carbon is present (that is, that  $K_1$  is zero and  $K_2$  be chosen so as to accord with the data on the solubility of graphite in iron). The single point for 50 per

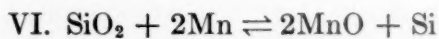
\* This equation implies that the homogeneous reaction producing  $\text{Fe}_3\text{Si}$  is endothermic; however, it is well known from plant experience in the making of silicon steel that the addition of ferrosilicon to molten steel is accompanied by a rise in temperature of the steel even though the ferrosilicon is cold. Furthermore, Körber and Oelsen<sup>12</sup> have shown the mixing of iron and silicon to be exothermic. The plant observations may be somewhat misleading in view of the oxidation that takes place simultaneously with the mixing—in fact, a "secondary slag" is noted on the ladle; however, Körber and Oelsen's results seem convincing. If the mixing of iron and silicon is truly an exothermic process, then the above equation is in error. Considering the excellent checks obtained at  $1600^\circ\text{C}$ . (shown on the following pages) it seems most likely that the source of error lies in disregarding compounds of silicon other than  $\text{Fe}_3\text{Si}$  at the lower temperatures and higher concentrations.



cent Si, as observed by Herty and Royer, fits in with this assumption better than with that previously made; but little weight is to be attached to this because it is likely that at such a high concentration the silicon is present in part as compounds containing more silicon than is in  $\text{Fe}_3\text{Si}$ , particularly at low temperatures, as mentioned above.

#### APPLICATION TO OTHER EQUILIBRIA

Oelsen recently published data<sup>1</sup> on the equilibrium at  $1600^\circ\text{C}$ . in the reaction



and expressed his results in the form of a "constant"  $K_6' = [\text{Si}^*]/[\text{Mn}^*]^2$ , which proved to be different in the different melts, whence he concluded that the law of mass action does not hold in these cases. His melts contained small concentrations of manganese and of silicon in liquid iron, nickel, cobalt, copper and in binary alloys of these elements with one another; the melts were made in silica crucibles, so that the oxide phase was saturated with respect to  $\text{SiO}_2$ , and consequently the activity of  $\text{SiO}_2$  was the same in all of them. Enough manganese was present to insure that  $\text{MnO}$  was the only oxide beside  $\text{SiO}_2$  present in significant concentration in the liquid oxide phase, and so the activity of  $\text{MnO}$  was also approximately the same in all cases. On this basis the proper equilibrium constant reduces to

$$K_6 = \frac{[\text{Si}]N}{[\text{Mn}]^2} \quad [6]$$

The previous discussion indicates that  $[\text{Si}^*]$  is not even nearly proportional to  $[\text{Si}]$ ; indeed, at low concentration in liquid iron at  $1600^\circ\text{C}$ ., the free silicon would be only about  $\frac{1}{60}$  of the total silicon, whereas in other elements this fraction would be very different, in copper perhaps nearly unity, as is indicated by the following considerations:

In Fe-Si-Mn-Y liquid alloys in which the element Y forms no compounds the expression for the Fe-Si equilibrium may be written in the form

$$\frac{[\text{Fe}_3\text{Si}]}{[\text{Si}]} = K_5 \left( \frac{[\text{Fe}]}{N} \right)^3$$

whence by adding unity to both sides, and combining with the preceding equation for  $K_6$

$$\frac{\text{Si}_M}{[\text{Mn}]^2} = \frac{K_6}{N} \left\{ K_5 \left( \frac{[\text{Fe}]}{N} \right)^3 + 1 \right\} \quad [6a]$$

If manganese forms no compound in the liquid, then  $[\text{Mn}] = \text{Mn}_M$ , and the left side of the foregoing may be written in terms of Oelsen's "con-

stant" as  $K_6' \frac{(\text{at.wt.Mn})^2}{(\text{at.wt.Si})}$ . Further if both  $\text{Si}_M$  and  $\text{Mn}_M$  are small—that is, present in dilute solution— $[\text{Fe}]$  may be replaced by  $\text{Fe}_M$ , and for

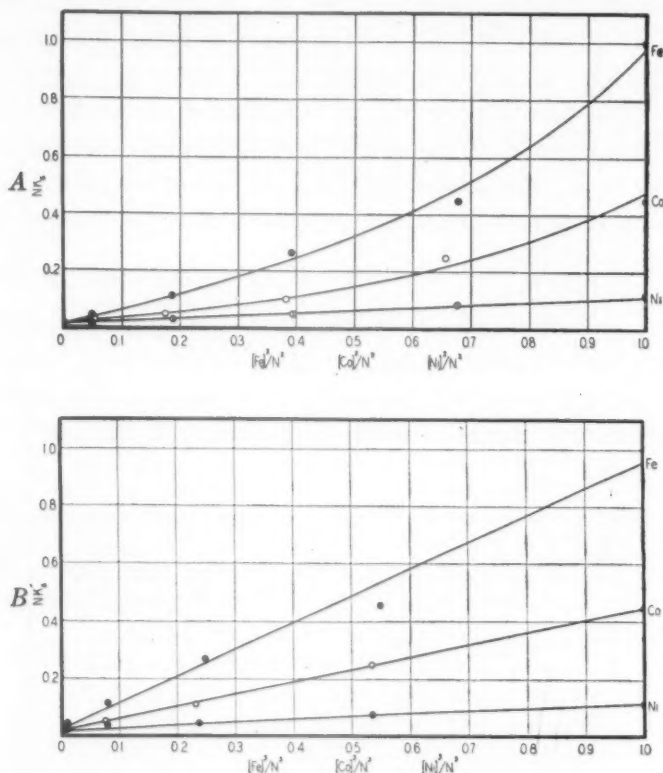


FIG. 3.—RELATION BETWEEN QUANTITY  $N \frac{[\text{Si}^*]}{[\text{Mn}^*]^2}$  AND MOL FRACTION OF IRON, COBALT, OR NICKEL IN MELTS OF IRON, COBALT OR NICKEL, AND COPPER WITH SMALL AMOUNTS OF SILICON AND MANGANESE IN  $\text{SiO}_2$  CRUCIBLES, SHOWING THAT REQUIREMENT OF LINEARITY DEMANDS CUBE (*B*) OF MOL FRACTION RATHER THAN THE SQUARE (*A*) BE USED AS ABSCISSA.

$N$  may be written  $\text{Fe}_M + Y_M$ . On this basis the foregoing equation becomes

$$(\text{Fe}_M + Y_M) K_6' \frac{(\text{at.wt.Mn})^2}{(\text{at.wt.Si})} = K_6 \left\{ K_5 \left( \frac{\text{Fe}_M}{\text{Fe}_M + Y_M} \right)^3 + 1 \right\}$$

which may be rearranged as follows

$$K_6' (\text{Fe}_M + Y_M) = \left\{ K_6 K_5 \left( \frac{\text{Fe}_M}{\text{Fe}_M + Y_M} \right)^3 + K_6 \right\} \frac{(\text{at.wt.Si})}{(\text{at.wt.Mn})^2} \quad [6b]$$

This equation expresses Oelsen's "constant"  $K_6'$  in terms of our constants  $K_6$  and  $K_5$  and concentration terms, and thus shows that  $K_6'$  cannot be constant if  $K_5$  and  $K_6$  are. It shows, moreover, that if Oelsen's data are plotted in the way suggested by the foregoing equation [namely,

$K_6'(\text{Fe}_M + Y_M)$  against  $\left(\frac{\text{Fe}_M}{\text{Fe}_M + Y_M}\right)^3$ , a linear relation should result, provided that  $K_6$  and  $K_5$  are themselves constant and that the index 3 (corresponding to the compound  $\text{Fe}_3\text{Si}$ ) is correct. As a matter of fact, when a series of plots was made, with indexes 2 and 3, the latter alone gave a straight line, as is shown by Fig. 3. Moreover, that index 1 does not give a straight line is evident from Oelsen's own mode of plotting, as in Fig. 4, which shows that the graph has marked curvature.

The values of  $K_6$  and of the product  $K_5K_6$  may be obtained directly from Fig. 3b, as they are the intercept and slope respectively multiplied by the factor  $\frac{(\text{at.wt.Mn})^2}{(\text{at.wt.Si})}$ . However, in order to secure a better value of each of these quantities,  $K_5K_6$  and  $K_6$ , we fitted to eq. 6b, by the method of least squares, all of Oelsen's data on the systems Fe-Cu, Co-Cu, Ni-Cu, the last two being treated by the same procedure as has been outlined for the Fe-Cu system: the results are as follows, it being noted that when X is iron  $K_X$  is  $K_5$ :

System	$K_6$ (from Intercept)	$K_XK_6$ (from Slope)	$K_X = \frac{[\text{X}_3\text{Si}]}{[\text{X}][\text{Si}]}$
Fe-Cu.....	2.3	101	51
Co-Cu.....	1.9	42	21
Ni-Cu.....	2.1	10.2	5.1
Cu.....	1.7		

The values in the column  $K_X$  are derived from the preceding column by dividing by the mean value of  $K_6$ ; namely, 2.0. The value so calculated for  $K_5$  is  $51 \pm 8$ ,\* which compares favorably with the value  $59 \pm 8$ , given on an earlier page, derived from the data on the solubility of graphite in liquid iron containing silicon. This agreement of values calculated from entirely independent sets of data is, we believe, a corroboration of the point of view adopted. This is also evident from Fig. 4, which shows Oelsen's experimental points in direct comparison with the curve drawn on the basis of eq. 6a, using the value of  $K_6$  derived from the Fe-Si-C system and of  $K_5$  as derived above. The agreement is all that could be expected.

Another quite independent corroboration is afforded by a comparison of data on the deoxidation of steel by silicon with this equilibrium, as

\* The  $\pm$  sign refers only to relative error; that is, it is a measure of the consistency of the results. As Oelsen's melts contained on the average about 1.4 per cent Mn and 0.4 per cent Si, the mol fraction of iron as calculated is in error by about 4 per cent and its cube consequently by about 12 per cent. If this correction is made,  $K_5$  would be larger by about 12 per cent, or would be about 57, fortuitously close to the value 59 derived from the data on the solubility of graphite in liquid iron.

derived from data in the literature and our value of  $K_5$ . The several equations are,\* for temperature about 1600°C. ( $T = 1873^\circ$ ):

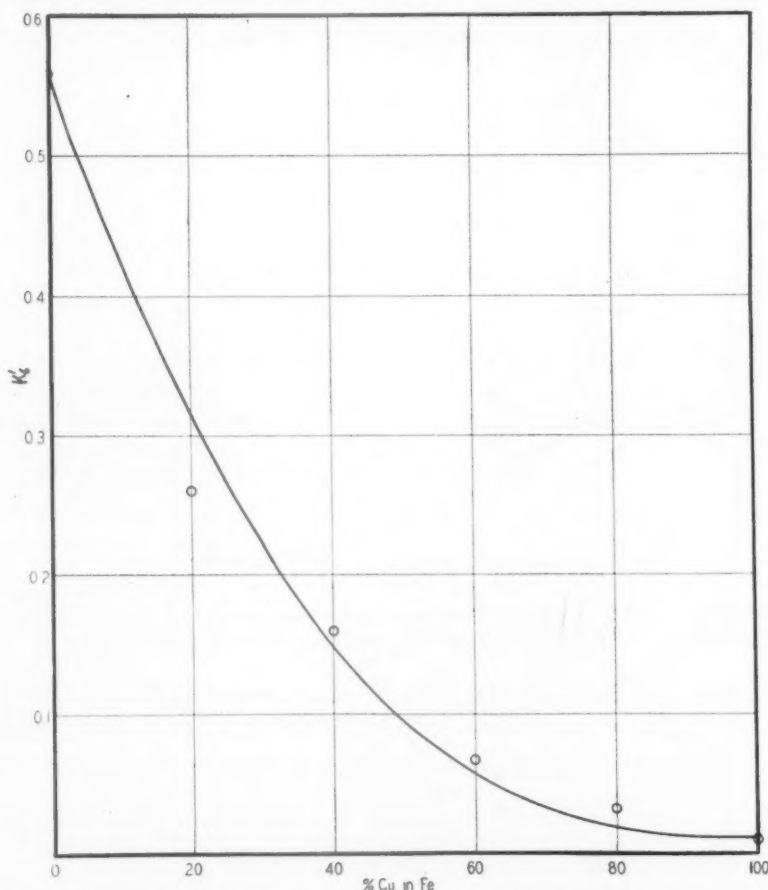


FIG. 4.—CALCULATED AND OBSERVED VALUES OF THE QUANTITY  $[\text{Si}^*]/[\text{Mn}^*]^2$  IN IRON-COPPER ALLOYS.

whence for iron or steel in equilibrium with solid  $\text{SiO}_2$

$$\log [\text{Si}^*][\text{FeO}^*]^2 = -43930/T + 20.24 \quad [7]$$

In Fig. 5 are compared on a plot of  $[\text{Si}^*]$  against  $[\text{FeO}^*]$  the curves derived for four temperatures by means of this equation, with points

\* A. As derived from  $K_5$ .

B. This value is derived from the heat data and entropies from the following sources: Kelly,<sup>13</sup> Roth and Becker,<sup>14</sup> Korber and W. Oelsen.<sup>12</sup>

C. Chipman and Samarin.<sup>15</sup> The values starred are in terms of percentage by weight, to afford direct comparison with the experimental values.

representing published experimental data of Körber and Oelsen,<sup>16</sup> of Herty and Fitterer,<sup>17</sup> as well as certain data from steelworks practice. All these data are in about as good agreement as could be expected, considering the large experimental error indicated by the scatter of the points. At least it is clear that if no compound formation between iron

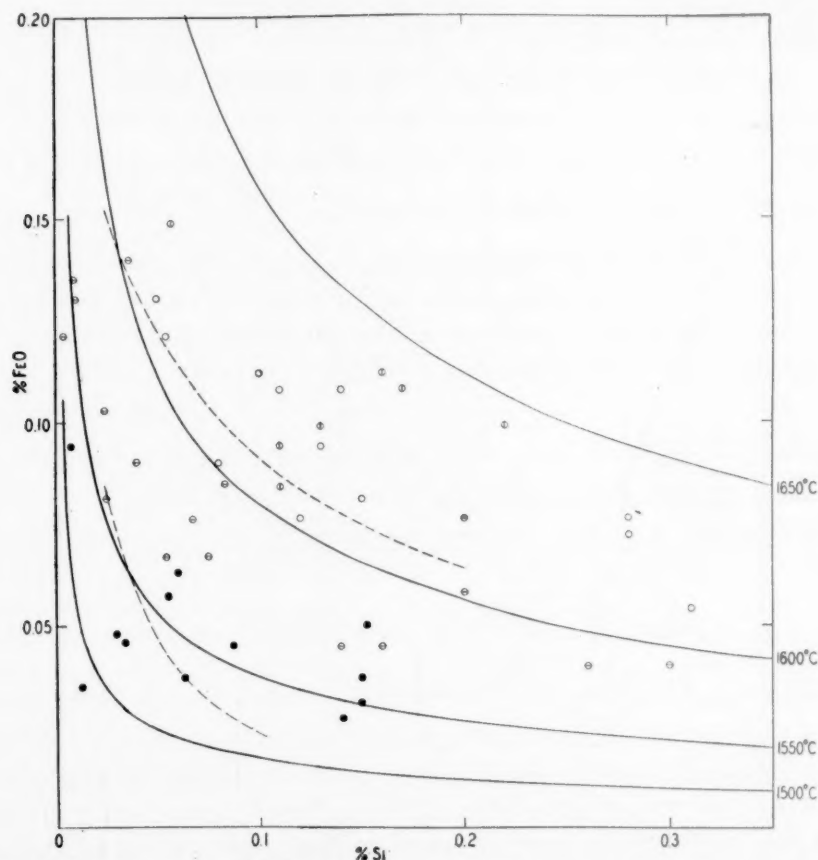


FIG. 5.—CALCULATED AND OBSERVED VALUES OF SILICON-IRON OXIDE EQUILIBRIUM IN MOLTEN STEEL.

Full curves, calculated values at temperatures shown.

Dashed curves, mean curves for plant values of 30 bath samples (upper curve) and 8 ladle samples (lower curve).

Open circles, Körber and Oelsen's values at the following temperatures: vertical cross bar, 1625° to 1680°; no cross bar, 1575° to 1625°; horizontal cross bar, 1530° to 1575°.

Solid circles, Herty's ingot samples.

and silicon had been considered, the calculated value of the deoxidation constant above would be decreased (at 1600°C.) to about  $\frac{1}{60}$  of that used in calculating the curves, and that then the curves would not fit the data at all.

#### APPLICATION TO DEOXIDATION OF STEEL

The relations of carbon and silicon in a liquid steel bath are evident from Fig. 6, which was constructed from the data of Fig. 5 and the table



by Chipman and Samarin<sup>18</sup> for the C-FeO equilibrium, and shows the calculated minimum value of the percentage of residual silicon required to prevent evolution of the oxides of carbon in the presence of solid SiO<sub>2</sub> (or ferrous manganese silicates containing over 50 per cent SiO<sub>2</sub>). This graph shows, for example, that a steel bath at 1600°C. containing 0.2 per cent C requires about 0.2 per cent Si to bring it to equilibrium with one atmosphere pressure of oxides of carbon. It is interesting that the curves clearly show that the higher the carbon the more silicon is required to prevent carbon monoxide evolution, although of course the equilibrium

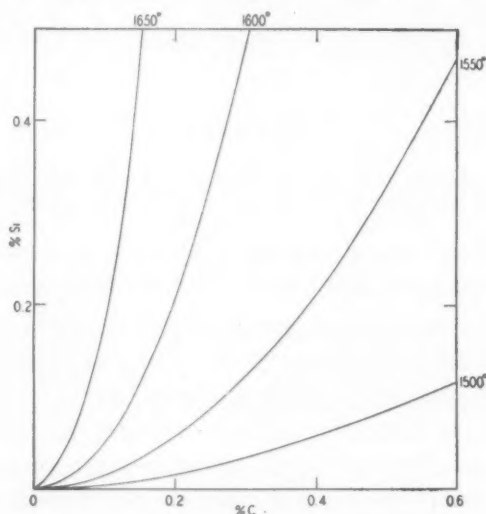


FIG. 6.—CALCULATED RELATION BETWEEN CARBON AND SILICON IN EQUILIBRIUM WITH SILICA AT ONE ATMOSPHERE PRESSURE AND AT THE INDICATED TEMPERATURES.

[FeO] is lower. These curves seem to be qualitatively in harmony with experience of what happens when a heat of steel is "blocked" by addition of silicon to prevent temporary loss of carbon as evolved CO and CO<sub>2</sub>. The amount of silicon required in practice, however, is likely to be lower than is indicated by the curves, because under the usual conditions of operation the reaction of FeO with carbon does not progress as far as equilibrium calculations indicate; also, perhaps to some extent because the silicon phase may be diluted with other oxides so that the activity of silica would not be unity, as is assumed in the calculated curves of Fig. 6. This latter influence is presumably secondary because, as is shown by Fig. 5, the equilibrium in the reaction  $2 \text{FeO} + \text{Si} \rightarrow 2 \text{Fe} + \text{SiO}_2$  (solid) is closely approached when silicon is used as deoxidizer.

Equation 7 and Fig. 5 show, moreover, that the product of the concentrations of Si and FeO in liquid steel in equilibrium with SiO<sub>2</sub> changes markedly with change of temperature—about fourfold for a rise of 50°C. An explanation of the effect of silicon on the rimming action of steel in molds cannot exclude the effect of a temperature coefficient as large as this. The phenomenon of rimming, which is essentially a deoxidation

by carbon, is more complex than this simple statement implies; for instance, undoubtedly there are differences of temperature and steep concentration gradients in the liquid close to the solid-liquid interface during freezing. In spite of these complications, and of the fact that the occurrence of the rimming action is probably not predictable merely from equilibrium data, it seemed worth while to make an approximate calculation of the relation between the concentration of silicon that would prevent rimming and the carbon content at the freezing temperature corresponding to this carbon content. The indications, derived on this basis, are that to prevent rimming the residual silicon in the steel would be higher the higher the carbon content. This deduction is in accord with observations by Cook<sup>19</sup> but does not seem to be generally recognized as valid in practice.

### SUMMARY

Application of the law of mass action to the homogeneous equilibria involving carbon and silicon in molten iron, on the assumption that the molecular species  $\text{Fe}_3\text{C}$  and  $\text{Fe}_3\text{Si}$  are present in such solutions, leads to a representation of the available data that brings them into substantial accord. These data include the solubility of graphite in liquid iron and in iron-aluminum and iron-silicon melts; the vapor pressure of the iron-carbon system at high temperatures and the  $\text{CO-CO}_2$  ratio in equilibrium with them; the heat of formation of iron carbide; the equilibrium between silicon and manganese in low-carbon molten steels and the respective oxides in the slag phase, and the deoxidizing characteristics of silicon.

The consistency of the results of the calculations is regarded as an indication that the use of the simple form of the law of mass action is justified in the treatment of data on solutions in liquid iron provided that compound formation in the liquid is taken into account. The interpretation proposed is not valid over the whole range of concentrations (over 15 per cent Si) in the iron-carbon-silicon liquid system, for it is probable that compounds other than  $\text{Fe}_3\text{Si}$  are present in appreciable concentrations at the higher silicon concentrations and at the lower temperatures. Although the method of treatment presented here leads to a consistent picture, which is in accord with a variety of experimental results, it is known to the author that at least one entirely different method of treatment leads to a correlation of experimental data that is essentially equally satisfactory. The validity of the extension of the method used here must depend on further and more accurate experimental data.

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## DISCUSSION

(John Chipman presiding)

J. CHIPMAN,\* Cambridge, Mass.—The calculations reported in this paper make possible a considerable simplification in the thermodynamic treatment of liquid solutions of carbon and silicon in iron. The concept of a molecular solute partly dissociated into its constituent atoms seems simple, and familiar in contrast to previous doubts as to the possibility of the existence of molecules in such solutions. The one serious drawback to the calculations is, as the author has indicated, that they indicate an absorption of heat when silicon reacts with liquid iron. This reaction actually is accompanied by an evolution of heat, even after the iron has been thoroughly deoxidized, and for this reason some modification of the calculations will be required. It would be interesting to know whether Dr. Darken has considered the possible formation of silicon carbide in a melt containing iron, carbon and silicon.

G. PHRAGMÉN,† Stockholm, Sweden.—It has been known for about 10 years that the carbon activity in a dilute solution of carbon in liquid iron is only about one-fifth part of the value deduced from the assumption of proportionality between the carbon activity and the atom fraction of carbon. This fact implies that there is some kind of affinity between carbon and iron. The observations may be explained with good approximation by the assumption that the liquid alloy is an ideal solution containing Fe, C and  $\text{Fe}_3\text{C}$ , the mol fraction of C being much lower than that of  $\text{Fe}_3\text{C}$ . But this is not proof of the existence of  $\text{Fe}_3\text{C}$  molecules in the solution. In fact, in the crystal structure of  $\text{Fe}_3\text{C}$  as determined by Westgren no molecules can be indicated. Every iron atom has two carbon atoms at the same distance and every carbon atom is surrounded by six iron atoms. When carbon dissolves in gamma iron, the number of iron atoms in the face-centered elementary cube retains its value 4, and the carbon atoms move into the interstices between the iron atoms. The largest interstitial room is in the center of the elementary cube, and a carbon atom in such a position is surrounded by six iron atoms at the same distance. The rapid diffusion of carbon in austenite is another indication that no stable carbide molecules are present.

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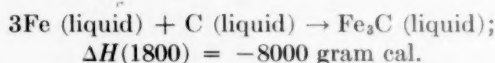
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† Metallografiska Institutet.

Probably the solution of carbon in liquid iron has a similar structure. From the atomic radii it may be inferred that the number of iron atoms in "contact" with a carbon atom will be six, as in the solid phases discussed. Probably these iron atoms are equivalent. It is also likely that the iron atoms surrounding a carbon atom are continuously replaced by other iron atoms. If this view is correct the chemical attraction between iron and carbon causes the carbon dissolved to be "solvated" without any real carbide molecules being formed.

The affinity between carbon and iron must be accepted as an experimental fact. Then one might expect that heat would be evolved when iron and carbon combine. One result of the author's calculations is inconsistent with this view; he has found that a rather large quantity of heat should be absorbed when graphite and liquid iron combine to liquid iron carbide. According to the usual assumptions about the heat contents of the reacting substances, it must be concluded, however, that if  $\Delta H(298) = 4400$  gram calories for the reaction  $3\text{Fe (solid)} + \text{C (graphite)} \rightarrow \text{Fe}_3\text{C (solid)}$ , probably  $\Delta H(1773)$  is negative; that is, heat is actually evolved at  $1500^\circ\text{C}$ . (compare discussion on p. 273). The value of  $\Delta H$  for the reaction  $\text{Fe}_3\text{C (in liquid Fe)} + \text{CO}_2 \rightarrow 3\text{Fe (liquid)} + 2\text{CO}$  is 40,080, according to Chipman, and not 28,800 as ascribed to him by the author (p. 210). Hence from Chipman's equations:  $3\text{Fe (liquid)} + \text{C (graphite)} \rightarrow \text{Fe}_3\text{C (in liquid Fe)}$ ;  $\Delta H = 40,130 - 40,080 = 50$ . Probably the heat of fusion of  $3\text{Fe}$  is of the same order of magnitude as that of  $\text{Fe}_3\text{C}$ , and we may take it as sure that the numerical value of  $\Delta H$  is small for the reaction  $3\text{Fe (liquid)} + \text{C (graphite)} \rightarrow \text{Fe}_3\text{C (liquid)}$ .

For estimating the affinity we need, however, the value of  $\Delta H$  for the fictive reaction  $3\text{Fe (liquid)} + \text{C (liquid)} \rightarrow \text{Fe}_3\text{C (liquid)}$ . The heat of fusion of graphite is not known; if its melting point is assumed to be  $3800^\circ\text{K}$ . it may be estimated to 8000 gram cal. per gram atom, according to a rule by Richards. If it is further assumed that the heat of transformation from the solid to the liquid state is the same at  $1800^\circ$  as at  $3800^\circ\text{K}$ ., we obtain as a rough approximation



Hence the mixing of the *liquids* is accompanied by an evolution of heat, which might account for the affinity observed.

It is beyond doubt that the mixing of iron and silicon is an exothermic process. The heat of mixing is so great as to cause a technically useful increase in temperature, as observed by Walter in 1921. By the simple method described by Körber and Oelsen in 1934, results have been found for other alloy systems, which coincide extremely well with results obtained by completely different methods.<sup>21</sup> The heat evolved when one gram atom of liquid silicon is mixed with a large quantity of liquid iron has been reported as 28,500 gram cal.; that is, half as much as when one gram atom of oxygen combines with iron. Such a great heat evolution cannot be attributed to errors in the method of observation.

Surely the heat of mixing cannot be so great without strong chemical forces between the components, and one must expect the activity of silicon and iron in the liquid alloy to be much lower than if it were an ideal solution of iron and silicon. The affinity probably is much greater than between iron and carbon, but there is still no proof of the existence of true compound molecules. When silicon dissolves in alpha iron, some iron atoms in the body-centered cubic lattice are replaced by silicon atoms; then every silicon atom is surrounded by eight iron atoms at the same distance. In the  $\text{FeSi}$  phase groups consisting of one iron and one silicon atom may be distinguished from the point of view of crystal symmetry, but still every silicon atom is surrounded

<sup>21</sup> Mitt. K.W.I. Eisenforschung, Düsseldorf (1937) 19, 209.



by four iron atoms at almost the same distance. In the phase  $\text{FeSi}_2$  no molecules are present, and every silicon atom has four iron atoms at the same distance. These facts do not make it plausible that real compound molecules are present in the liquid iron-silicon alloys.

The heat of mixing of iron and aluminum is even greater than that of iron and silicon, hence it is very likely that the iron has a strong affinity for aluminum; that is, the activity of iron will be much less than the atomic fraction. The author has found that the solubility of graphite in iron-aluminum alloys may be explained by the assumption that iron, carbon and aluminum form an ideal solution, containing molecules  $\text{Fe}$ ,  $\text{C}$ ,  $\text{Fe}_3\text{C}$  and  $\text{Al}$ . This assumption is improbable because of the great heat of mixing mentioned, and it may also be expected that aluminum has a considerable affinity for carbon; the carbide  $\text{Al}_4\text{C}_3$  is well known and its formation from aluminum and graphite is a highly exothermic process.

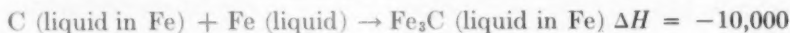
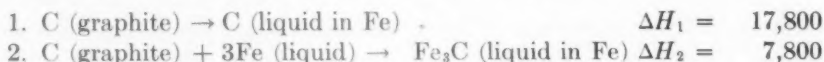
L. S. DARKEN (author's reply).—Dr. Chipman's and Dr. Phragmén's remarks regarding the exothermic nature of the reaction between silicon and iron in the molten state are well taken. The author regards this as an indication of defeat in the interpretation adopted in this paper. However, the heat of solution of molten aluminum in liquid iron is also reported as large yet Chipman (ref. 2) finds (not in disagreement with the present paper) that the deviation from ideality (compared to carbon and silicon) is small. It appears to the author that an actual measurement such as this can be given far more weight than the rather loose reasoning of Phragmén on this point.

The author did not intend to imply anything about the microstructure of solutions of the various alloying elements in liquid iron. The solution of the problem by the methods of statistical mechanics has never been developed, and until that time comes we shall have no insight into the microstructure of metallic melts; however, if it is possible by a few relatively simple mathematical assumptions to interpret a number of macroscopic or thermodynamic properties, that method may be useful even though it tells us nothing of the behavior of individual atoms and the forces operating between them.

The value 28,800 cal. used in this paper is for the heat of the reaction  $\text{Fe}_3\text{C}$  (solid in austenite) +  $\text{CO}_2$  (gas)  $\rightarrow$   $3\text{Fe}$  +  $\text{CO}$  (gas) and is taken from Chipman (ref. 2). It is not used as a heat for the reaction involving liquid  $\text{Fe}$  and  $\text{Fe}_3\text{C}$ , as stated by Phragmén, but is combined as stated with other appropriate heats to obtain heat data for reactions involving the liquids.

The rule of Richards (that the entropy of fusion of the elements is about 2.1 entropy units) is frequently in gross error, particularly in the zone between metals and nonmetals. The entropy of fusion of the elements varies with position in the periodic table. If the entropy of fusion of graphite be taken the same as that of silicon (5.6 e.u.) the heat fusion of graphite calculated therefrom is  $3,900 \times 5.6 = 21,800$  cal. per mol, which is in fair agreement with the value 17,800 given for  $\Delta H$ .

It is interesting to note that by subtracting eq. 1 from eq. 2 an equation is obtained for the homogeneous reaction mentioned by Phragmén:



This is in astonishing agreement with the value  $-8000$  calculated by Phragmén from hypothesis contradictory to the above.



## The Solubility of Nitrogen in Molten Iron-silicon Alloys

BY J. C. VAUGHAN, JR.,\* AND JOHN CHIPMAN,† MEMBER A.I.M.E.

(Chicago Meeting, October 1939)

ALTHOUGH a considerable amount of practical importance attaches to systems involving gases and molten metals, little is known regarding the effects of alloy elements upon the solubility of gases in liquid iron. The solubilities of hydrogen<sup>1</sup> and nitrogen<sup>2,3</sup> in pure liquid iron are known and it has been shown that small amounts of silicon and aluminum<sup>3</sup> exert only a small effect upon the solubility of nitrogen but greatly increase its rate of solution.

This paper presents the results of a study of the solubility of nitrogen, at pressures approximately one atmosphere, in molten iron containing up to 15.8 per cent silicon.

### EXPERIMENTAL METHOD

There are two general methods by which the solubility of a gas in a molten metal may be determined. In the first, which Sieverts<sup>1</sup> employed, the gas is measured from a burette into the enclosure containing the metal and the amount absorbed is found by subtracting from the total volume that of the dead space in the container. The second method, which was used successfully for pure liquid iron, is to expose the molten metal to the gas until absorption ceases, then to solidify and analyze the metal. In either method the stirring produced by inductive heating prevents the development of a stagnant layer at the metal surface and ensures actual attainment of equilibrium. Obviously the second method is accurate only when the saturated metal is capable of solidifying without gas evolution. Since the rate of solution of nitrogen in iron is increased by the presence of silicon, it was to be expected that the rate of evolution would be correspondingly increased and for this reason the first method was selected.

A sketch of the furnace is shown in Fig. 1. A small high-frequency coil having 17 turns fitted closely around a fused silica tube, 2 in. in diameter, in which was placed, on a bed of 60-mesh alumina sand, an

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Manuscript received at the office of the Institute July 5, 1939. Issued as T.P. 1109 in METALS TECHNOLOGY, October 1939.

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<sup>1</sup> References are at the end of the paper.

alundum thimble of 1-in. inside diameter containing the metallic charge. Around the thimble was poured alumina sand, which served to fill space, decrease radiation loss, and support the thimble in a vertical position. The sand used was carefully measured in a graduated cylinder; the same amount was used each time, and was not packed down; consequently conditions were fairly uniform for each run, and the blanks made were applicable throughout. The sand was cleaned with acid and thoroughly washed after using, and could be employed over and over; but a new thimble was required for each run. Frequent acid-cleaning of the silica tube was also necessary, to remove the coating of sublimed metal. A molybdenum ring cut from 0.012-in. sheet, with an outside diameter of 1 in. and a  $\frac{1}{2}$ -in. hole, was suspended by molybdenum wire to a level

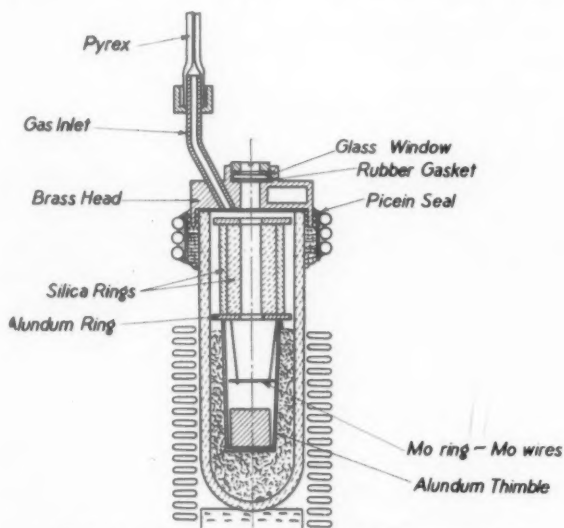


FIG. 1.—FURNACE USED IN EXPERIMENTS.

about  $\frac{1}{2}$  in. above the surface of the metal, in order to prevent bridging of the charge. The ring became very brittle; some molybdenum was vaporized; and a small amount of metal from the charge condensed upon it. It cracked on occasions, and had to be replaced regularly. Several alundum disks, drilled to  $\frac{1}{2}$  in. in the center, and two concentric fused silica rings about 2 in. high were employed as space fillers, resting on top of the thimble. The disks were renewed each time, while distilled metal made necessary the cleaning of the silica rings after every run.

A water-cooled brass head, providing an inlet tube for nitrogen and a glass window held tightly against a rubber gasket by a threaded brass piece, was cemented to the top of the silica tube by means of Picein wax, which was kept cool by a copper coil mounted on a brass sleeve and connected to the silica tube by zinc-silicate cement. A skirt on the head dipped into the wax about  $\frac{1}{2}$  in., and, although the original sealing job was often troublesome, no leaks ever developed during a run.

The nitrogen supply was tank nitrogen, 99.8 per cent pure, and practically free of argon. It was purified by passing it through two glass tubes containing copper lams at  $500^{\circ}\text{C}$ ., and a drying tower containing phosphorus pentoxide. A tube packed with surgical cotton removed any  $\text{P}_2\text{O}_5$  that might be blown from the drying tower. From this tube the nitrogen entered the gas burette, which had been calibrated over its entire length by mercury weighing. A side tube opening to the air through a bubbling bottle made it possible to flush the purification train with nitrogen before filling the burette. Mercury was used to displace the gas in the burette. Instead of a leveling bulb, an aspirator bottle set above the level of the top of the burette, and connected through stopcocks to the air and to a vacuum line, was employed. After a fair amount of practice it became a simple matter to control the mercury level and the pressure in the burette. A side tube of the same diameter as the burette, and connected to it and to the mercury supply at the bottom, was used to indicate the gas pressure.

From a two-way stopcock at the top of the burette, glass tubing ran to the nitrogen supply and to the furnace. The line to the furnace was of 1-mm. capillary tubing, since it was desirable to cut the volume to a minimum. Two side lines ran off from the capillary tube, one through a stopcock to a vacuum pump, the other to a mercury manometer.

The volume of the gas space inside the furnace and connecting tubing was found to be 125 c.c., and this volume was kept constant throughout the series of experiments by controlling the size of the charge and the amount of alumina packing. The "hot volume" or the amount of gas measured at room temperature required to fill the furnace containing a molten charge was, of course, very much less than this and was subject to variation with the temperature of the charge. Using liquid nickel, which was found to dissolve virtually no nitrogen, this volume was found to be 58 c.c. at  $1500^{\circ}$  and 55 c.c. at  $1650^{\circ}\text{C}$ .

Two iron-silicon alloys were prepared by melting electrolytic iron and commercial silicon (98.5 per cent) in a magnesia crucible under an atmosphere of hydrogen. The charges were made up by appropriate amounts of these alloys, which contained, respectively, 0.005 and 15.83 per cent silicon.

Temperatures were measured with a "Pyro" optical pyrometer, which was checked frequently at the melting point of iron. There was no difficulty in obtaining accurate temperature measurements as long as the melt was in vacuum, but during the absorption a considerable amount of smoke was formed, which condensed on the sight glass and made accurate measurement impossible.

The procedure in carrying out a determination was as follows: A weighed amount (75 grams) of iron-silicon alloy was placed in the crucible, which was then inserted in the tube and surrounded by a measured

volume of alumina sand. The molybdenum disks and other furnace parts were placed, the cover cemented on and the furnace was evacuated. The charge was melted in vacuum and thoroughly outgassed until no pressure rise could be observed on the manometer when the stopcock between pump and furnace was closed for a 5-min. period.

Nitrogen was admitted rapidly from the burette until the furnace pressure reached atmospheric, after which the pressure was maintained constant and frequent burette readings were recorded. Since the heat loss from the metal is greater in nitrogen than in vacuum it was necessary to increase the power input slightly just before the gas was admitted.

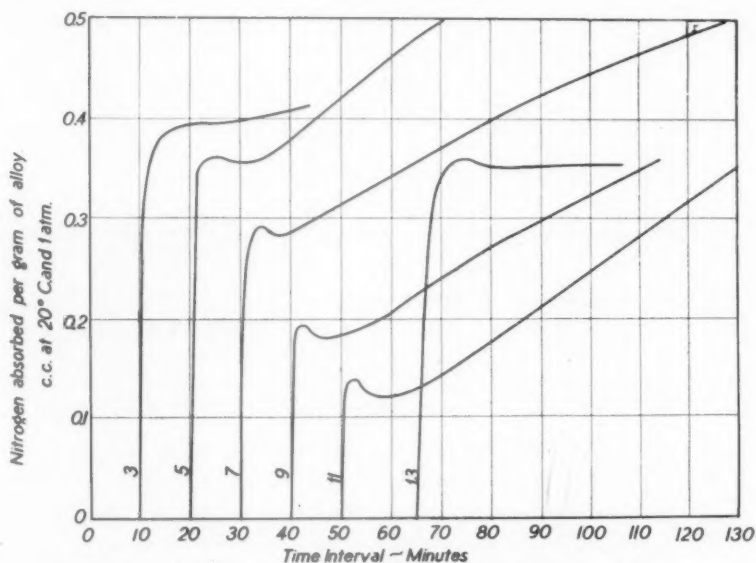


FIG. 2.—ABSORPTION CURVES OF REPRESENTATIVE RUNS.

Within 10 min. after the gas was admitted, the sight glass became fogged and further temperature measurements were impossible. During the first 10 min. of the absorption period, therefore, it was necessary to adjust the power input to produce the desired temperature, after which the power was held constant for the remainder of the run. This procedure was based upon experience gained with silicon-free melts that did not fog the window. The temperature control was much less certain than could have been desired. It was estimated that all the melts except No. 4, which was hotter, were made between 1600° and 1660° C.

The absorption curves of representative runs are shown in Fig. 2. The rate of absorption of nitrogen during the first few minutes was extremely rapid in all melts that contained silicon. Within a few minutes, absorption ceased and was followed by an apparent evolution of gas. This strange behavior was at first attributed to fluctuation of temperature in the furnace but in the light of our theoretical explanation of the results,



which will be discussed later, it now seems possible that in some cases an actual evolution of gas occurred as a result of the restoration of equilibrium following an initial supersaturation.

This period was followed by a prolonged slow absorption of gas, which, however, never occurred in the absence of silicon. The rate of this absorption was practically constant as long as the metal was molten, extending in some cases as long as 3 hr. It appeared that this slow absorption was not taking place in the melt itself but in the distilled metal above the melt. Enough of this material was collected for analysis and was found to contain 0.21 per cent nitrogen. The slow absorption was always accompanied by the appearance of smoke in the furnace and tentatively both phenomena may be ascribed to the formation and condensation of silicon nitride.

The best values for the solubility of nitrogen in the melt will be taken as the minimum points in the curves of Fig. 2. These points are recorded in the third column of Table 1.

TABLE 1.—*Experimental Data on Solubility of Nitrogen in Iron-silicon Alloys at 1600–1660° C.*

Heat No.	Silicon, Per Cent	Nitrogen, Per Cent		
		Total Absorbed	Evolved	Analysis
1	0.28	0.042		
2	0.66	0.046	0.011	0.030
3	1.19	0.046	0.008	0.031
4	2.01	0.049	0.008	0.026
5	2.52	0.041	0.004	0.023
6	3.34	0.0355	0.008	0.017
7	3.99	0.0325	0.006	0.018
8	5.19	0.0275	0.009	0.014
9	7.53	0.021	0.007	0.013
10	9.79	0.014	0.000	0.014
11	12.45	0.014	0.000	0.006
12	15.83	0.0082	0.000	0.005
13	0.001	0.041	0.002	
14	0.004	0.037	0.000	

During the solidification of each melt, burette readings were taken at  $\frac{1}{2}$ -min. intervals in an effort to determine the amount of gas evolved. These readings, plotted against time, showed an offset at the moment of solidification, which was small when no gas was evolved and fairly large when gas evolution was pronounced. From the shapes of the curves, an estimate of the amount evolved was obtained and recorded in the fourth column of Table 1. The solidified metal was cut vertically into repre-



sentative segments, which were analyzed for silicon and nitrogen, the latter by vacuum fusion; the results are recorded in the table. It is probable that during cooling some gas was evolved from the metal while it was yet in the liquid state and for this reason the sum of the fourth and fifth columns of the table is not expected to agree precisely with the third column, which is considered the most probable value of the actual solubility.

### INTERPRETATION OF RESULTS

The initial increase in nitrogen solubility followed by an abrupt decrease was, to say the least, unexpected. The simplest explanation that can be offered is briefly the following: In liquid iron, nitrogen dissolves as a compound containing several atoms of iron and one atom of nitrogen per molecule. The activity of iron is greatly diminished by

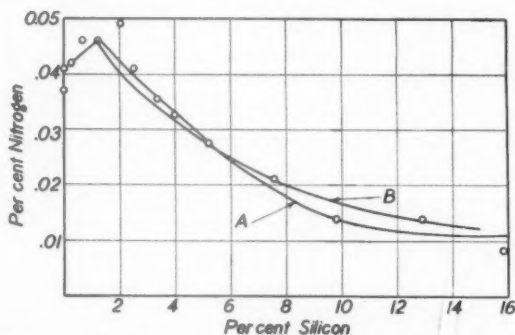


FIG. 3.—COMPUTATIONS VERSUS EXPERIMENTAL RESULTS. Curve A represents  $\text{Fe}_3\text{Si}$  and  $\text{Fe}_6\text{N}$ ; curve B,  $\text{FeSi}$  and  $\text{Fe}_8\text{N}$ .

silicon, probably by formation of a compound, and the decrease in nitrogen solubility from about 2 per cent silicon onward is due to the decrease in free iron in the solution. The initial increase in solubility is the result of the formation of a silicon nitride of limited solubility in the melt. The maximum in the solubility curve occurs when the silicon content is sufficient to form this nitride; further increases in silicon content exert a negligible effect upon the amount of silicon nitride dissolved.

These hypotheses are in agreement with other known facts regarding the elements concerned. An iron nitride containing one atom of nitrogen accounts for the proportionality of its concentration to the square root of pressure. Silicon dissolves in liquid iron with evolution of heat and its activity is less than would be expected for an ideal solute.<sup>4</sup> Silicon and nitrogen form several nitrides, one of which at least is fairly stable at 1600° C. From the data of Hincke and Brantley<sup>5</sup> the dissociation pressure of  $\text{Si}_3\text{N}_4$  at this temperature is only about 16 mm. Finally, the coincidence of the break in the rate-of-solution curve with formation of smoke in the apparatus is interpreted as the precipitation of solid silicon

nitride from the liquid iron solution and its gradual volatilization and condensation in colder parts of the furnace.

It is interesting to speculate on the nature of the compounds of iron and silicon and of iron and nitrogen, and the data provide the basis for such a speculation, although they are not sufficiently precise to permit a unique solution.

The simplest numerical method of approach is to assume a formula for the iron silicide, compute the mol fraction of free iron at several concentrations and determine the power to which this must be raised to parallel the curve, which in turn fixes the formula that must be ascribed to the iron nitride. The amount of nitrogen dissolved as iron nitride is then calculated at several percentages of silicon; above the peak of the curve a constant solubility of silicon nitride is assumed and the sum of the two gives the total nitrogen solubility. Up to the peak, which is taken as 1.2 per cent silicon because of experimental uncertainties in the point at 2 per cent, the amount of silicon nitride is taken proportional to the percentage of silicon.

The results of two such computations are shown in Fig. 3 in comparison with the experimental results, which are shown as circles. Curve *A* corresponds to  $\text{Fe}_3\text{Si}$  and  $\text{Fe}_6\text{N}$  while curve *B* represents  $\text{FeSi}$  and  $\text{Fe}_3\text{N}$ . Although curve *A* represents the data somewhat more closely than any other combination we have tried, it is evident that other possible combinations lead to results that also fit the data within the limits of experimental error.

The nature of the compounds that occur in the solid state unfortunately throws no light upon the constitution of the liquid solution. We would not be justified in preferring curve *B* to curve *A* because of the stability of  $\text{FeSi}$  and the nonoccurrence of  $\text{Fe}_3\text{Si}$  in the solid state. It is of interest in this connection that Darken,<sup>6</sup> in a study of the iron-carbon-silicon system, has found that the solubility of graphite in liquid iron-silicon alloys can be satisfactorily represented on the basis of the occurrence of  $\text{Fe}_3\text{Si}$  in the melt.

#### ACKNOWLEDGMENTS

The authors wish to express their thanks to Mr. T. E. Burke, who calibrated the gas burette and carried out preliminary determinations of solubility that were substantially in agreement with those reported in this paper.

#### SUMMARY

The solubility of nitrogen at atmospheric pressure in liquid iron-silicon alloys containing up to 15.8 per cent silicon has been determined at  $1630^\circ \pm 30^\circ \text{C}$ . The solubility increases from 0.041 per cent in pure

iron to about 0.046 per cent between 1 and 2 per cent silicon, then decreases to about 0.01 per cent at the highest silicon concentration employed. The results indicate the formation of an iron nitride and an iron silicide in solution and a silicon nitride of limited solubility in the melt.

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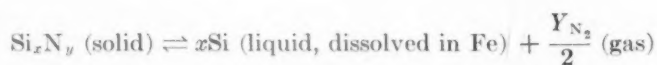
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## DISCUSSION

(C. Y. Clayton presiding)

L. S. DARKEN,\* Kearny, N. J.—It is interesting to note that the postulate of  $\text{Fe}_3\text{Si}$  in Fe-Si melts is in accordance with the experimental data here presented. That this postulate has been found to accord with the results of many researchers will be shown soon in a publication from this laboratory.

The explanation of the maximum nitrogen solubility at about 1.2 per cent Si does not seem quite clear. Application of the phase rule to this system shows immediately that at equilibrium three phases (melt, gas and solid silicon nitride) cannot coexist over a finite range of composition (at fixed temperature and pressure). From the equations



$$\frac{p_{\text{N}_2}^{y/2} a_{\text{Si}}^x}{a_{\text{Si}_x\text{N}_y}} = K$$

it is clear that if the pressure of nitrogen and the activity of solid silicon nitride be fixed (as presumably they were) the activity and hence the concentration of the dissolved silicon is fixed; i.e., at concentrations of silicon above the value corresponding to saturation with a solid silicon nitride, this nitride would tend to separate out until the silicon concentration was reduced, presumably to the 1.2 per cent value. Since this did not occur the system was not in complete equilibrium (at least, under the hypothesis of the presence of a solid silicon nitride). The melts may have been in equilibrium (or nearly so) with either the nitrogen gas or the solid nitride, but not both. If the melts were in equilibrium with nitrogen gas, no break in the curve would occur; whereas if the melts were in equilibrium with the solid nitride (at silicon concentrations above 1.2 per cent) the fact that the experiments were run at one atmosphere pressure of nitrogen is of no significance and the part of the curve beyond the break can be regarded as the solubility of silicon nitride in molten iron.

J. B. CAINE,† Lockland, Ohio.—The question of the evolution of nitrogen as a gas when iron or steel solidifies has created a great deal of controversy in the past.

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† Sawbrook Steel Castings Co.

Some investigators have found no evolution of nitrogen on solidification, while others have found just the opposite.

The results given in Table 1 for evolved nitrogen, showing the very marked effect of silicon dissolved in the iron, may be the reason for this disagreement.

Although the curve shown in Fig. 3 for total nitrogen absorbed shows a maximum at about 1 per cent Si, the amount of evolved nitrogen shows a much more pronounced maximum at about 0.66 per cent Si, for with very low silicon contents there is no evolution of nitrogen.

Could the authors verify these data by giving some information as to whether the ingots were porous and if there was any relation between this porosity, the silicon content and the evolved nitrogen?

N. F. TISDALE,\* Pittsburgh, Pa.—It is indeed surprising to note the effect of silicon on the solubility of nitrogen in iron. I am interested to know whether Dr Chipman has determined the effect of other alloys, such as molybdenum, nickel, chromium, etc., on the solubility of nitrogen. It is reasonable to suppose that some other alloys must have an effect of reducing the solubility of nitrogen in iron and if he has not done any of this work I would like to suggest that he give it some consideration for future work.

J. CHIPMAN (author's reply).—Dr. Darken is correct in his application of the phase rule. At a given temperature solid silicon nitride can exist in equilibrium with the melt and with one atmosphere pressure of nitrogen at only one composition of the metallic phase. We were unable to detect solid silicon nitride on the surface of any of the melts but postulated its formation, either in the gas phase or on the metal surface from which it subsequently volatilized, as the explanation of two observed phenomena; namely, the formation of smoke and the protracted absorption of gas after the melt had apparently become saturated. The nature of this absorption is still far from clear but of one thing we can be certain, its rate is extremely slow compared to the initial rapid absorption of nitrogen. This makes it possible for the melts to have been substantially in equilibrium with gaseous nitrogen but far from equilibrium with respect to this secondary process. In the absence of dependable data on the stability and vapor pressure of silicon nitride the exact nature of this secondary absorption cannot be deduced. It must be admitted, however, that our interpretation of the results can be valid only if this compound has some appreciable vapor pressure at the temperature of the experiments.

Mr. Caine's question regarding nitrogen evolution is an interesting one. We have observed that small amounts of silicon or aluminum accelerate gas evolution on solidification and it may be assumed that the reason for this is closely tied to the mechanism by which these same elements hasten its absorption. In the present series all melts up to and including No. 9 evolved gas and the resulting ingots were porous. There was, however, very little difference in the degree of porosity from one ingot to another. Those above 9 per cent Si were quite sound. The actual amount evolved could not be measured accurately, especially when solidification occurred over a range of temperature as in the higher silicon alloys. It would be difficult to say where the maximum evolution occurs but if we judge by the difference between the amount absorbed and that retained in the ingot, the heats containing between 2 and 3 per cent Si evolved the greatest amount of gas.

In answer to Mr. Tisdale's question: We have done no experimental work on the solubility of nitrogen in other alloys of iron. The apparatus has been remodeled to improve its precision and is being used to study solubility of gases in molten copper. We hope later to return to the interesting problem of nitrogen in ferrous alloys.

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\* Molybdenum Corporation of America.



## Formation of Inclusions in Steel Castings

BY WALTER CRAFTS\* AND JOHN J. EGAN,\* MEMBERS A.I.M.E., AND W. D. FORGENG\*

(New York Meeting, February 1940)

ALTHOUGH many elements reduce the tendency to porosity in steel castings, manganese, silicon, aluminum, calcium, titanium and zirconium appear to be most generally suitable for the purpose. The manganese and silicon contents are usually maintained in a fairly constant range. Silicon-killed castings often are made to be sound with little or no addition of the stronger degasifiers. In many cases, however, it is more practical to utilize the stronger degasifying elements, aluminum, calcium, titanium and zirconium. Since they greatly modify the composition, shape, and distribution of the nonmetallic inclusions, and thereby the ductility, the strong deoxidizers must be used in such a way as to form the least harmful types of inclusions. As the reasons for failure always to obtain good results have not been obvious, an effort has been made to determine the mechanism of solidification of steels deoxidized to produce certain types of inclusions. Diagrams representing the mechanism of their formation have been constructed from the appearance of the nonmetallic constituents and have not only illustrated the limiting features of specific deoxidizing treatments with respect to inclusion formation and ductility, but have also indicated a relation between inclusions and resistance to hot tearing.

Three different types of deoxidation treatment have been used for obtaining sound castings with relatively high ductility. The first method is to make and cast the steel under such conditions that deoxidation with silicon and a small addition of a strong deoxidizer assures soundness. The effective addition that will promote soundness without causing the formation of intergranular inclusions varies with the furnace practice and composition, but may be limited to about 0.025 per cent Al, Zr or Ti. Up to 0.10 per cent Ca and 0.15 per cent V are also used for this purpose. The inclusions in these steels are characteristically glassy silicates and round or irregular sulphides. As pointed out by Sims and Lillieqvist,<sup>1</sup> the formation of fine intergranular inclusions, which are detrimental to ductility, limits the amount of strong deoxidizers that may be added.

Manuscript received at the office of the Institute Dec. 1, 1939. Issued as T.P. 1184 in METALS TECHNOLOGY, April 1940.

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<sup>1</sup> References are at the end of the paper.



The second type of treatment is the large aluminum addition suggested by Sims and Dahle.<sup>2</sup> The amount of aluminum added (0.10 to 0.20 per cent) is sufficient to cause the separation of an immiscible oxide phase and to form a minimum of harmful eutectic inclusions. Average ductilities reported by Sims and Dahle for grade B steel castings were as shown in Table 1.

TABLE 1.—*Average Ductilities of Grade B Steel Castings*

Typical Inclusions	Type <sup>a</sup>	Approximate Aluminum Addition, Per Cent	Elongation in 2 In., Per Cent	Reduction of Area, Per Cent
Silicate.....	I	None	30	49
Eutectic.....	II	0.05	23	35
Alumina.....	III	0.10	27	42

<sup>a</sup> Designation used by Sims and Dahle.

A third type of treatment has been described by Grotts,<sup>3</sup> in which the high-aluminum addition of Sims and Dahle is supplemented by treatment with calcium-silicon. The average results of tests under commercial conditions in which the steel was treated with 0.125 to 0.175 per cent Al were reported to be as given in Table 2.

TABLE 2.—*Average Results of Tests under Commercial Conditions*

Deoxidation	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent	Reduction of Area, Per Cent
Plain.....	43,000	72,000	29.2	46.2
Ca-Si.....	45,350	74,000	31.2	54.2

Similar results were obtained by Gagnebin<sup>4</sup> when using an intermediate (0.06 per cent) aluminum addition together with calcium, zirconium or beryllium under special conditions of oxidation and order of additions.

The present inclusion study included the examination of both commercial steels and steels made at the Union Carbide and Carbon Research Laboratories. The experimental heats of the latter were made in a basic high-frequency furnace crucible, starting with a low-carbon charge. No slag was carried and all additions were made in the crucible. This practice resulted in a metal somewhat more oxidized than comparable commercial steel. In some tests calcium alloys were added either in the form of loose lumps or wrapped in a light perforated sheet-steel capsule that was plunged into the metal. Unless otherwise noted, the steels contained approximately 0.30 to 0.35 per cent C, 0.75 to 1.00 per cent Mn, 0.015 per cent P, 0.035 per cent S, and 0.35 to 0.50 per cent Si. Some

heats were also made in the ranges of 0.005 to 0.010 per cent and 0.050 to 0.060 per cent S.

Typical mechanical properties of double-keel block castings made according to the different types of deoxidation treatment outlined above are given in Table 3. The steels were normalized from 925°C., annealed from 900°C., and drawn at 200°C. for 24 hours.

TABLE 3.—*Mechanical Properties of Castings*

Deoxidizing Additions, Per Cent		Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent	Reduction of Area, Per Cent
Al	Ca				
	0.10	41,000	78,500	32.0	57.0
0.05		44,000	78,000	17.5	36.5
0.10		50,000	75,750	27.5	40.4
0.10	0.10	49,500	82,000	30.0	50.0

## INCLUSION SOLIDIFICATION DIAGRAMS

Various degrees of deoxidation produce different kinds, shapes, and arrangements of inclusions, and these differences have been utilized to construct diagrams illustrating the solidification process. For this purpose five inclusion types have been chosen, corresponding to types resulting from graduated additions of aluminum, and in one test, calcium. No effort has been made to review all possible kinds of three-component systems likely to be found. Three types: silicate, alumina and peritectic, correspond to the three common deoxidation treatments described

TABLE 4.—*Types of Inclusions*

Type	Aluminum Addition, Per Cent	Ductility	Nonmetallic Inclusions <sup>a</sup>
Silicate.....	0.025	Very good	Glassy silicates, round sulphides, and (intergranular sulphide films).
Eutectic.....	0.05	Poor	(Alumina), round sulphides and intergranular sulphide films.
Galaxy.....	0.075	Poor	Alumina, round sulphides and (intergranular sulphide) films or oxide galaxies.
Alumina.....	0.10	Fairly good	Alumina, round sulphides and (intergranular sulphide films or oxide galaxies).
Peritectic.....	0.10 (0.05 Ca)	Good	Alumina, duplex, round sulphides, and (intergranular sulphide films).

<sup>a</sup> Parentheses indicate appearance only in small amounts.

above, and the eutectic and galaxy types represent intermediate undesirable conditions. The types of inclusions found in typical steels treated with graduated amounts of aluminum are indicated in Table 4.

The metal-oxide-sulphide type of ternary solidification diagrams that have been constructed on the basis of these inclusion types have been previously used by Benedicks and Löfquist<sup>5</sup> and Wentrup<sup>6</sup> to illustrate roughly quantitative diagrams of simple systems of iron and nonmetallics. The data for such basic diagrams are extremely limited, and the presence of carbon, manganese, silicon, aluminum, etc., as well as lack of equilibrium conditions, makes it impossible to construct quantitative solidification diagrams for the nonmetallics in deoxidized steel. The compositions of the oxide and sulphide phases under various conditions of deoxidation are not known, and knowledge of the pertinent oxide-sulphide systems is inadequate. However, efficient use of deoxidizing elements has demanded rough working diagrams even though they are wholly qualitative and limited to specific conditions. A series of diagrams has been prepared on the basis of the inclusion types described in Table 4. Obviously, the "binary" and "ternary" systems illustrated are only simplified conjectural representations of the complex systems that are actually present in steel.

Certain assumptions have been necessary in order to interpret the mechanism of formation of inclusions from their appearance, shape, size and distribution. In addition, the extrapolation from a limited oxide-sulphide ratio to a "ternary" metal-oxide-sulphide diagram has entailed assumptions regarding the metal-oxide, metal-sulphide, and oxide-sulphide "binary" diagrams. The construction was also simplified by ignoring the delta-gamma peritectic reaction in iron. The oxide-metal system was considered to have an extended miscibility gap, and for convenience the eutectic was placed near the oxide rather than the metal phase. The sulphide-metal system is also shown with a range of limited solubility. While the diagrams have been constructed with respect to deoxidation with aluminum, examination of the inclusions in steels treated with titanium or zirconium has indicated, with the exceptions below, very similar mechanism of solidification.

In constructing the solidification diagrams (Figs. 2, 5, 8, 11, and 14), the different kinds of inclusions have been classified with respect to their mechanism of formation according to the following assumptions:

1. Random oxides (silicate or alumina) are formed at a liquid miscibility gap.
2. Round sulphides and oxide particles distributed in a rough network formation are formed as binary eutectics between metal and sulphide, and metal and oxide, respectively. In higher aluminum steels, translucent round sulphides are formed as a binary eutectic between metal and an oxysulphide compound.



3. Intergranular fine sulphides represent a ternary eutectic between metal, sulphide, and oxide or oxysulphide compound.

4. Galaxies, or clusters of oxide particles, similarly represent a ternary eutectic between metal, oxide, and oxysulphide compound.

5. Duplex inclusions having a geometrically shaped oxide core and sulphidelike periphery are formed by an incompleting peritectic transformation from oxide to oxysulphide compound.

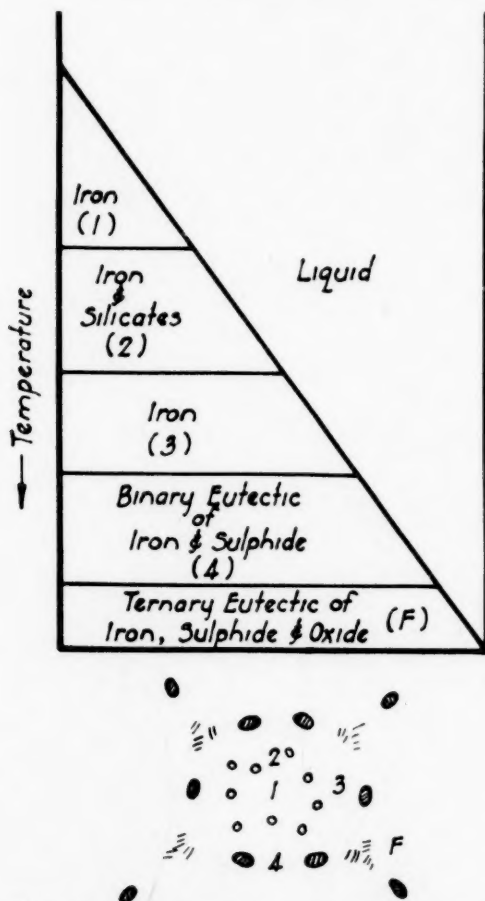


FIG. 3.—ORDER OF SOLIDIFICATION OF TYPICAL STEEL OF THE SILICATE TYPE.

tively, silicate, sulphide eutectic, oxide galaxy, alumina and peritectic.

#### SILICATE TYPE

Steels of the medium-carbon type deoxidized with 0.25 to 0.50 per cent Si contain inclusions of the types illustrated in Fig. 1 when treated without a strong deoxidizer or with not more than about 0.025 per cent Al, Ti or Zr, or up to 0.10 per cent Ca. Glassy silicates distributed at random are associated with round or irregular gray sulphide inclusions distributed in an incomplete network type of formation. The network is often poorly defined and is not sufficient to impair the ductility. The

By the nature of their construction, the diagrams obviously illustrate only the specific steels studied, even though the data have been extrapolated to form ternary diagrams to assist in understanding the manner of solidification. Further, it cannot be emphasized too strongly that the diagrams not only are not quantitative but are conjectural in many respects. They have been constructed to serve as a guide to the deoxidation of steel castings and have answered several anomalies and indicated more effective means of utilizing deoxidizers.

In the following paragraphs are described the mechanisms of solidification that have been inferred from observation and classification of the character of the inclusions in steels deoxidized in such a way that the predominant inclusion types are, respec-





FIG. 4.—TYPICAL INCLUSIONS IN STEEL OF THE EUTECTIC TYPE.

<i>a</i>	<i>b</i>	<i>c</i>
a. Binary eutectic oxides.    × 500.		
b. Continuous intergranular ternary eutectic.    × 250.		
c. Disconnected intergranular ternary eutectic.    × 500.		

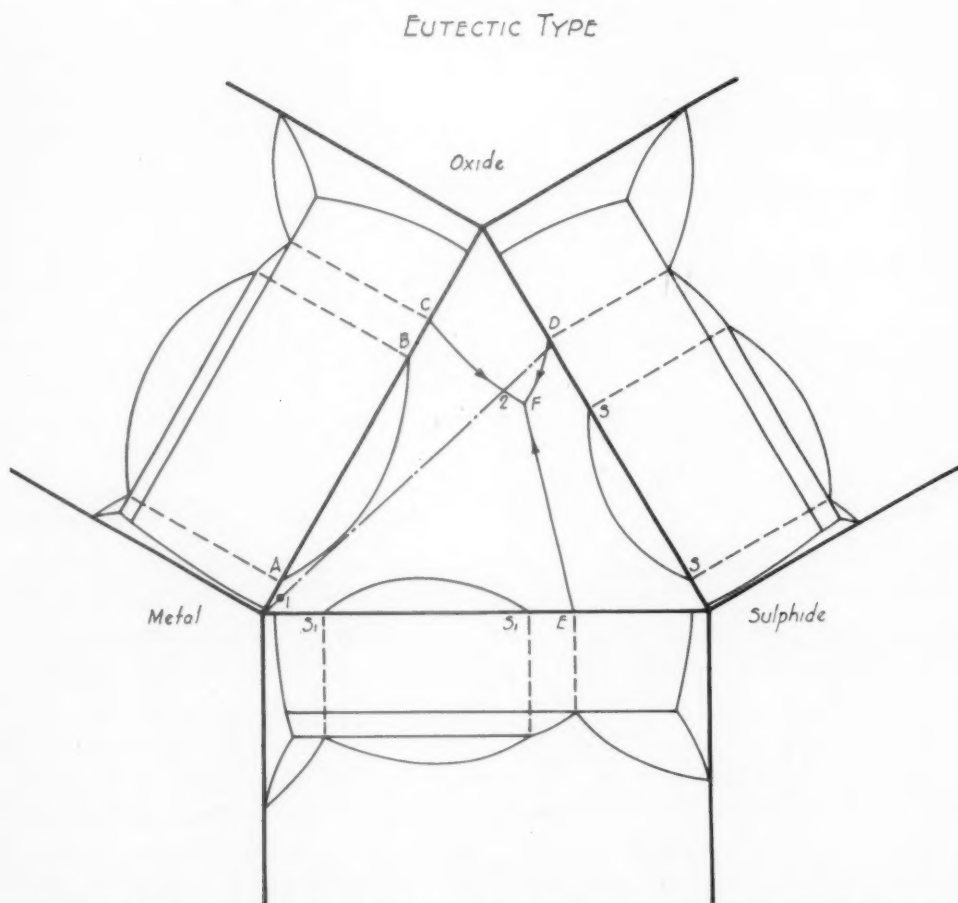


FIG. 5.—TERNARY SOLIDIFICATION DIAGRAM FOR STEEL OF THE EUTECTIC TYPE.

reduction of area is usually well in excess of 50 per cent in steel of the silicate type that has been carefully made to avoid porosity.

The ternary diagram derived from the inclusions in steel of the silicate type is shown in Fig. 2. The presence of random silicates is reflected in

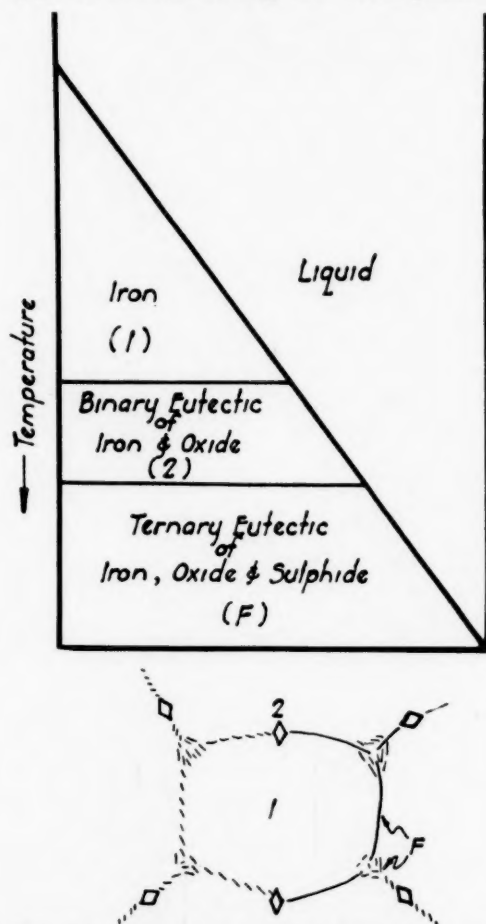


FIG. 6.—ORDER OF SOLIDIFICATION OF TYPICAL STEEL OF THE EUTECTIC TYPE.

metal and sulphide (4, *F*), and finally a small amount of ternary eutectic between metal, oxide and sulphide. A schematic arrangement of inclusions in one primary grain that would be formed by this solidification process is also illustrated in Fig. 3.

#### EUTECTIC TYPE

If an addition of aluminum, titanium or zirconium is made to steel of the silicate type in sufficient quantity to change the character of the inclusions, the initial result is a decrease in the amount of silicate inclusions with corresponding increase in the fine intergranular sulphides and loss of ductility. The amount of aluminum required to produce this condition is about 0.05 per cent in the medium-carbon steel produced

an extended miscibility gap on the metal-oxide side of the diagram and the oxide-sulphide binary diagram contains a eutectic and a range of limited solubility. The amount of intergranular sulphide inclusions representing solidification at the ternary eutectic point *F* is very small in the silicate type of steel because of the large amount of nonmetallics rejected in the silicate immiscibility range (*A*, 2, 3, *B*).

The progress of solidification of the steel indicated by the dot and dash line in Fig. 2 is also shown schematically in Fig. 3. This composition represents the medium-carbon steel produced under the conditions described above. It is believed that the progress of solidification is first the precipitation of metal at 1, and then, in progression, metal and immiscible silicate particles (2, 3), metal (3, 4), round sulphides at the binary eutectic of

in the Laboratories. As shown in Fig. 4, the inclusions are also changed by formation of some oxide particles arranged in a poorly defined network. The disconnected intergranular sulphides represent a commoner form of the ternary eutectic than the continuous film (Fig. 4).

As indicated in Fig. 5, the reduction or elimination of a randomly distributed oxide (silicate) phase is presumably due to restriction of the metal-oxide miscibility gap. The appearance of binary oxide eutectic inclusions also seems to indicate a shifting of the composition of the ternary eutectic to a higher sulphur content. As indicated by the dot and

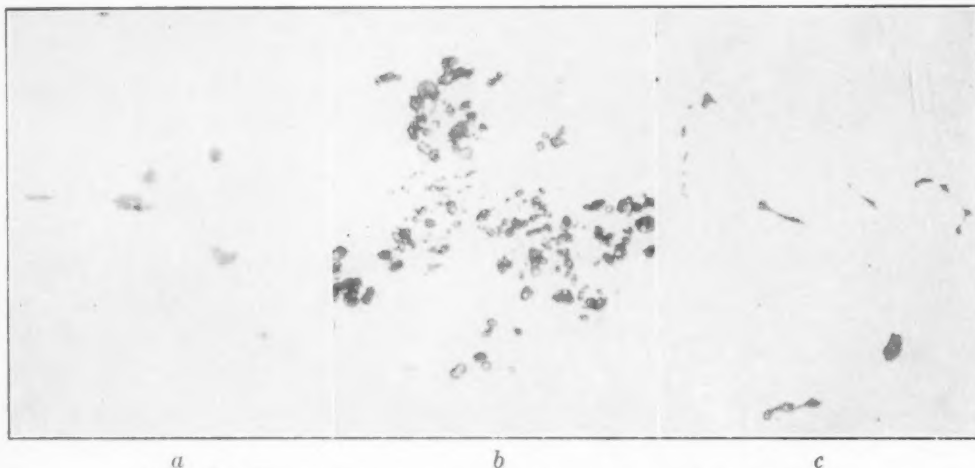


FIG. 7.—TYPICAL INCLUSIONS IN STEEL OF THE GALAXY TYPE.  
*a.* Binary eutectic sulphides.  $\times 500$ .  
*b.* Ternary eutectic oxide galaxy.  $\times 500$ .  
*c.* Intergranular ternary eutectic.  $\times 250$ .

dash line of Fig. 5 and by Fig. 6, the solidification of the typical steel would be characterized by initial freezing of the bulk of the metal (1, 2), a small precipitation of binary oxide-metal eutectic (2, *F*) and separation of most of the nonmetallic materials as the ternary metal-oxide-sulphide eutectic at *F*.

#### GALAXY TYPE

When the aluminum addition to the steel is raised to 0.075 per cent, there is a tendency toward compact grouping of the "alumina" particles in clusters or "galaxies" numbering from a few to thousands (Fig. 7). As suggested by Oberhoffer, Schiffler and Hessenbruch,<sup>7</sup> they appear to form as a ternary oxide eutectic. In Fig. 8 it has been assumed that an oxysulphide compound is formed in the oxide-sulphide system, in order to explain the presence of intergranular ternary sulphide eutectic inclusions in similar steel of higher sulphur content. In some steels, probably owing to segregation, both oxide galaxies and intergranular sulphides are sometimes encountered.



sulphur intergranular ternary eutectic sulphide inclusions. In addition to the strikingly different appearance of the two ternary eutectics, the binary eutectic oxysulphide inclusions formed near the oxide eutectic, which with ordinary illumination in the microscope have an appearance indistinguishable from rounded gray sulphides, tend to appear translucent under polarized light.

Oxide galaxy inclusions do not appear to be quite as harmful to ductility in the tensile test as the intergranular sulphides. A limited study of hot tearing, using a dumbbell specimen, has indicated that atmospheric oxidation produces eutectic inclusions at the surface of the casting. The intergranular sulphide form of the ternary eutectic has been found to be more prone to allow hot tearing than the oxide galaxy form. The presence of the galaxy eutectic adjacent to the oxide phase makes the galaxy type of steel less sensitive to hot tearing than the silicate or eutectic types.

#### ALUMINA TYPE

When the aluminum addition is increased to 0.10 per cent, an appreciable restoration of ductility is produced. Under ideal conditions the inclusions consist of randomly distributed alumina and round sulphides (oxysulphides) in a network formation as illustrated in Fig. 10. If the composition of the steel is unbalanced or the deoxidizing addition is not well diffused, the steel tends to contain either oxide galaxies or intergranular sulphides. As in Figs. 11 and 12, the mechanism of solidification is believed to be similar to that of the galaxy type except for the more extended metal-oxide miscibility gap and formation of randomly distributed "alumina" particles. Because of this early separation of nonmetallic material the amount of ternary eutectic inclusions tend to be small.

Sims and Dahle<sup>2</sup> showed that the high (0.10 to 0.20 per cent) addition of aluminum was most effective in producing high ductility in the lower sulphur steels. It is believed that this may be explained by a transition

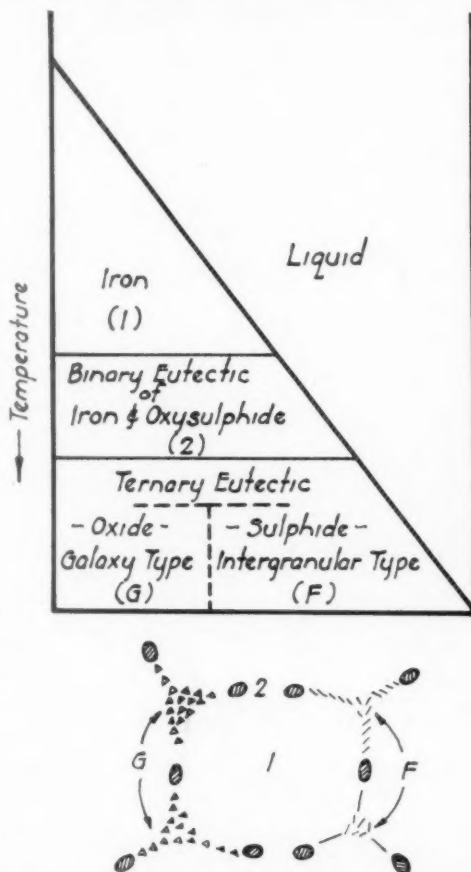


FIG. 9.—ORDER OF SOLIDIFICATION FOR TYPICAL STEEL OF THE GALAXY TYPE



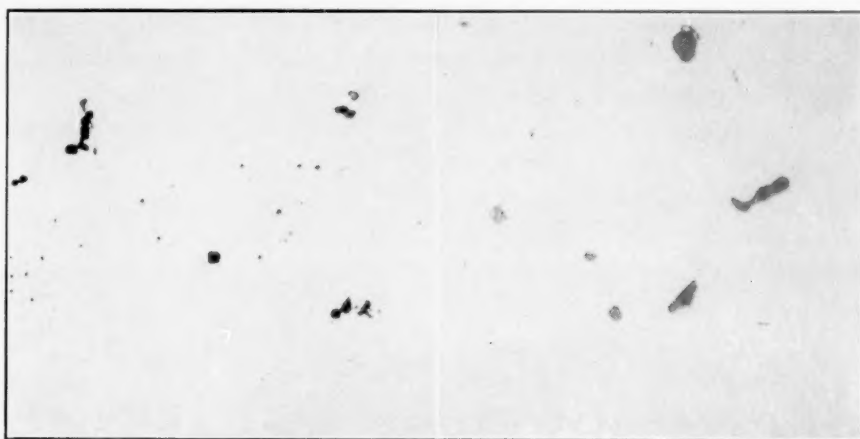


FIG. 10.—TYPICAL INCLUSIONS IN STEEL OF THE ALUMINA TYPE.  
 a. Immiscible "alumina."  $\times 100$ .  
 b. Binary eutectic oxysulphides.  $\times 500$ .

### ALUMINA TYPE

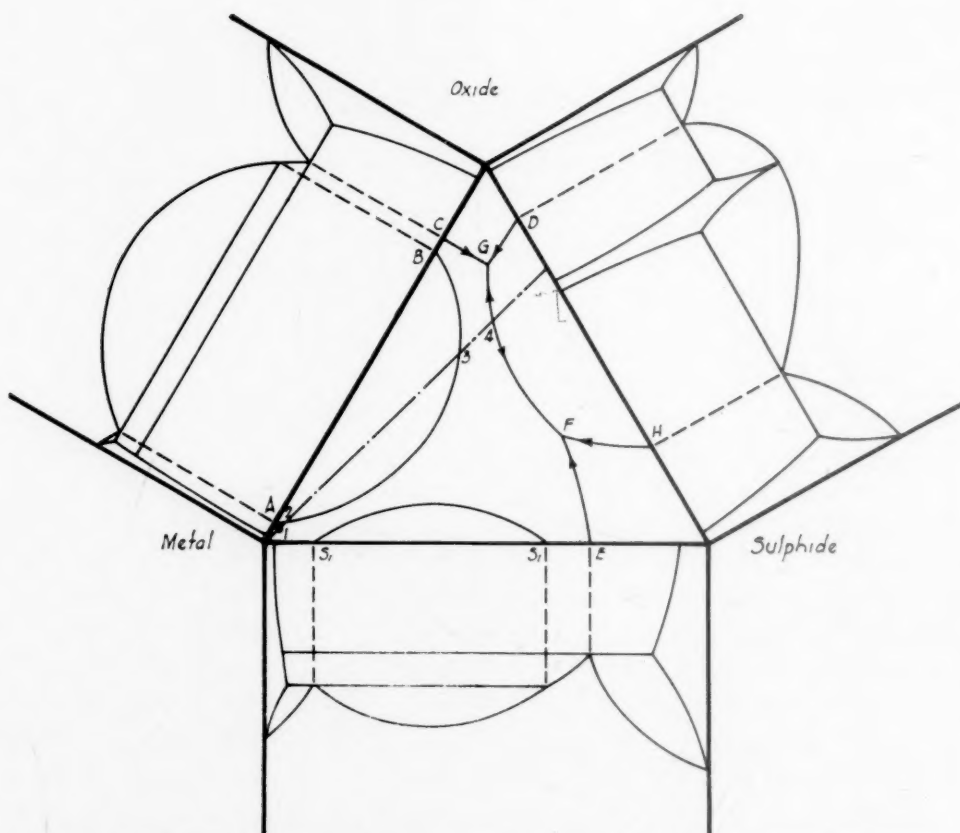


FIG. 11.—TERNARY SOLIDIFICATION DIAGRAM FOR STEEL OF THE ALUMINA TYPE.

from the tendency to form a ternary eutectic of intergranular sulphide inclusions in higher sulphur steels to the tendency to form the less harmful oxide galaxy ternary eutectic in lower sulphur steels. It may, therefore, be considered that there is a critical sulphide to oxide ratio that will produce optimum ductility after deoxidation with 0.10 to 0.20 per cent Al. The optimum composition is probably the highest ratio of sulphide to oxide that will permit the maximum amount of inclusions to be formed as binary eutectic between metal and oxysulphide, with assurance that the last material to solidify will be rich in oxide rather than in sulphide. Inasmuch as the relatively oxidized steels under consideration tend to form a small amount of galaxy inclusions at 0.035 per cent S, the critical amount of sulphur in this case is believed to be in the neighborhood of 0.040 per cent.

The inclusions formed by deoxidation with titanium (0.10 to 0.15 per cent) indicate that it has a critical sulphide to oxide ratio very nearly the same as that found with aluminum. Zirconium additions (0.10 to 0.15 per cent), on the other hand, produce at 0.035 per cent S a greater amount of galaxy inclusions than do aluminum or titanium. The critical sulphur content has not been established as accurately as for aluminum but appears to be slightly in excess of 0.050 per cent S for the zirconium-

treated experimental steels. A limited number of commercially produced steels have been examined and no great divergence from these critical values has been observed. On account of differences in composition and degree of initial oxidation, however, it is doubted whether the indicated critical sulphur contents are of general significance.

#### PERITECTIC TYPE

Calcium-bearing alloys added to steel receiving an addition of 0.10 to 0.20 per cent Al, Ti or Zr produce duplex inclusions having an angular, idiomorphous core surrounded by sulphidelike material (oxy-

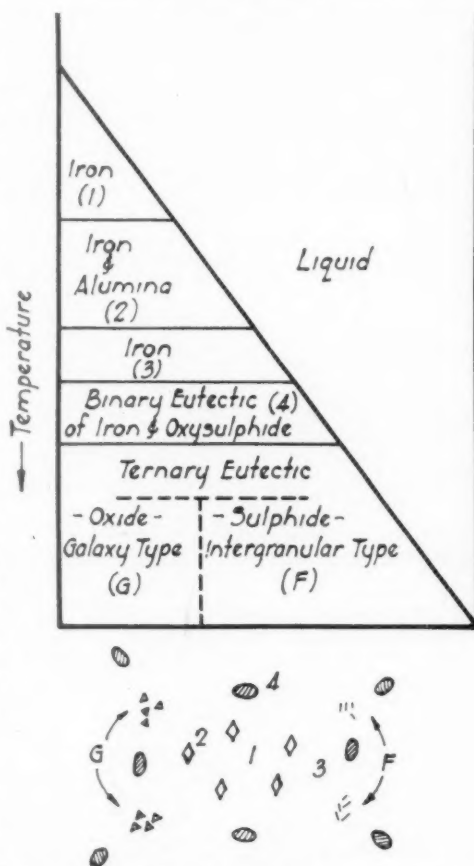


FIG. 12.—ORDER OF SOLIDIFICATION OF TYPICAL STEEL OF THE ALUMINA TYPE.

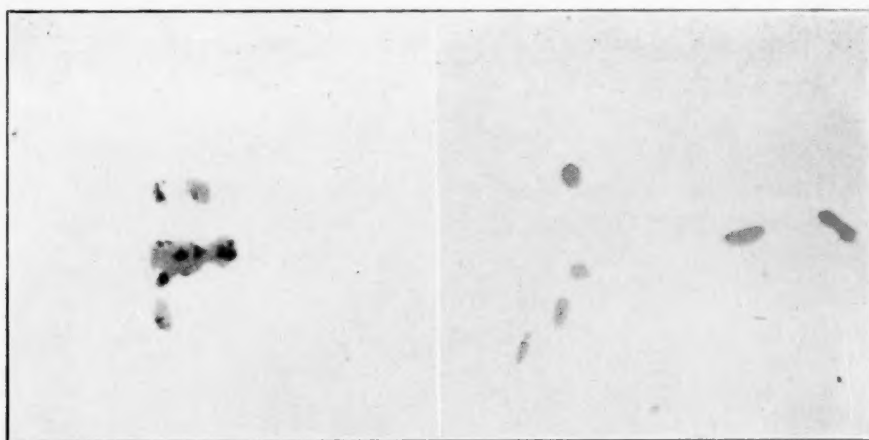


FIG. 13.—*a* *b*  
TYPICAL INCLUSIONS IN STEEL OF THE PERITECTIC TYPE.  
*a*. Peritectic oxysulphides.  $\times 750$ .  
*b*. Binary eutectic oxysulphides.  $\times 500$ .

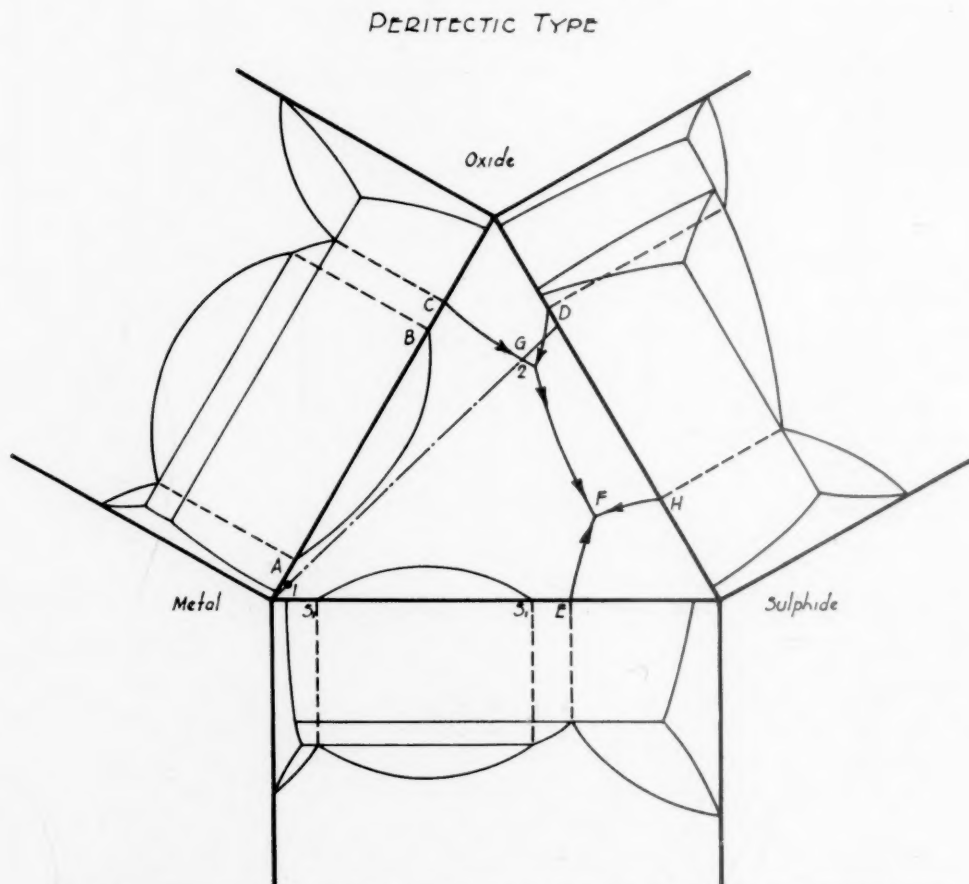


FIG. 14.—TERNARY SOLIDIFICATION DIAGRAM FOR STEEL OF THE PERITECTIC TYPE.

sulphide compound). In varying degree, depending on the amount and efficiency of the calcium addition, the duplex inclusions tend to become more numerous and the oxide galaxies tend to disappear. The steel treated effectively with aluminum and 0.05 to 0.10 per cent Ca has inclusions similar to those shown in Fig. 13.

As indicated by the oxide-sulphide binary diagram in Fig. 14, it is assumed that the duplex inclusions are formed by a peritectic reaction in which the oxide core does not have an opportunity to be entirely converted to oxysulphide compound. Occasionally oxysulphide inclusions are found that seem to confirm this hypothesis, as they do not have the dark oxide core but are, nevertheless, more translucent at the center than at the periphery. Both duplex inclusions and round sulphides tend to form in a network and, as indicated in Figs. 14 and 15, both are shown to separate as binary eutectics.

Probably by reason of elimination of galaxy inclusions, the ductility of steels of the peritectic type is usually superior to that of the alumina type. The addition of calcium with the aluminum, titanium or zirconium makes the sulphur content less critical and provides a buffer against irregularities in distribution of the deoxidizer that might lead to formation of galaxies in zones of relatively low deoxidizer content. Steels of the peritectic type seem to have the same degree of resistance to hot tearing that has been found in the strongly deoxidized steels that are not treated with calcium. Typical properties of experimental steels containing about 0.035 per cent S are given in Table 5.

#### SUMMARY AND CONCLUSIONS

A series of schematic diagrams has been presented to illustrate the mechanism of formation of nonmetallic inclusions in steel castings treated with graduated amounts of strong deoxidizers. In reconstruction

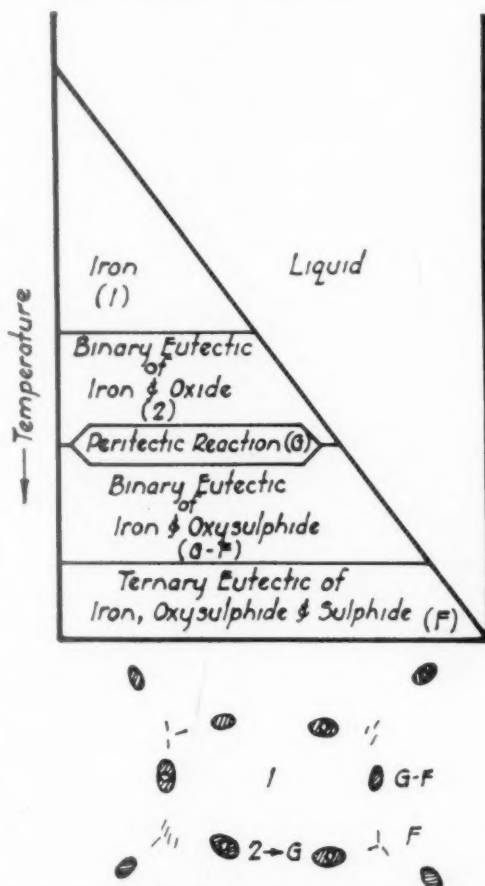


FIG. 15.—ORDER OF SOLIDIFICATION OF TYPICAL STEEL OF THE PERITECTIC TYPE.

of the mechanism of solidification from the character of the nonmetallic inclusions in steel castings, the most important, and least well substantiated, assumption is that large additions of aluminum, titanium and zirconium produce a separate, additional phase in their respective oxide-sulphide systems that has been designated as an oxysulphide compound. However, the metallographic evidence for the existence of such compounds appears to be convincing. The two different forms of ternary eutectic (oxide galaxy and intergranular sulphide) would indicate two ternary systems divided by the quasibinary system of metal and oxysulphide compound. The presence of an oxysulphide compound between the oxide and sulphide phases in the oxide-sulphide "binary" system is also predicated by the formation in calcium-treated steels of inclusions that appear to have been formed by a peritectic reaction.

TABLE 5.—*Typical Properties of Experimental Steels*  
0.035 PER CENT SULPHUR

Deoxidizing Additions, Per Cent					Yield Point Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent	Reduction of Area, Per Cent	Izod Ft.-lb.
Ca	Al	Zr	Ti	V					
0.05	0.10				53,000	77,500	27.0	44.9	30.5
0.05		0.10			46,000	78,000	27.0	42.2	32.5
0.05			0.10		45,500	74,500	26.5	38.8	25.3
0.05	0.075	0.075			47,000	75,500	28.5	44.0	35.0
0.05	0.075		0.075		53,000	79,750	27.5	45.2	32.0
0.05	0.05	0.05	0.05		51,300	77,500	29.0	48.2	33.0
0.05	0.075			0.075	51,000	78,500	28.5	48.9	37.3
0.05	0.04	0.04	0.04	0.04	52,500	77,000	29.0	49.5	38.0

The references to such an aluminum oxysulphide compound are summarized by Mellor<sup>8</sup> and are typified by the studies of Gautier,<sup>9</sup> who reported the formation of an aluminum oxysulphide compound as a result of action by hydrogen sulphide on aluminum oxide. The subject does not appear to have been studied very critically and no data suitable for the construction of the aluminum oxide-aluminum sulphide equilibrium diagram have been located in a search of the literature. Inconclusive studies have been made by the present authors on commercially purchased aluminum sulphide and on material prepared by treatment of molten aluminum with sulphur. Although all samples were contaminated with oxygen, at least one different atomic lattice structure has been found, in addition to that of alumina and that reported by Hanawalt, Rinn and Frevel<sup>10</sup> for aluminum sulphide. The possibility of allotropic forms of sulphide has not been eliminated, and it is considered that formation of an aluminum oxysulphide compound has not been firmly established. In spite of the uncertainty, however, it is believed that the appearance of the inclusions in the steel is sufficient to justify, for



the present purpose, the assumption of the presence of an oxysulphide compound in steels treated with large (0.10 to 0.20 per cent) amounts of aluminum, titanium or zirconium.

In summarizing the implications of the solidification diagrams, it should be emphasized that the metallographic observations of the inclusions were qualitative, that the derived empirical diagrams are both simplified and not quantitative. The high ductility usually obtained in steel of the silicate type when treated with large (0.10 per cent) additions of calcium is understandable, as calcium does not appear to form inclusions of the oxysulphide compound type and has only a minor influence on the intergranular sulphide ternary eutectic. The proneness to hot-tearing of steels of the silicate and eutectic types is also explained by the absence of the oxysulphide compound as a buffer between atmospheric oxidation and the intergranular eutectic, which seriously lowers the resistance of steel castings to hot-tearing. Conversely, the alumina and peritectic types are relatively resistant to hot-tearing at the oxidized surface owing to the formation of separated oxide particles rather than continuous intergranular films.

It is obvious from the diagrams that a close balance is required in steels of the alumina type to maintain high ductility by avoiding either oxide galaxies or intergranular sulphides. The maximum sulphur content that is permissible for good ductility has been indicated to be in the range of 0.040 per cent for the experimental steels treated with high aluminum or titanium, and slightly above 0.050 per cent for steels treated with zirconium. In the interest of economy the minimum effective amount of strong deoxidizer (about 0.10 per cent) is usually added, and the necessity for thorough diffusion to avoid oxide galaxy and intergranular sulphide inclusions is obvious. For this reason the more dilute and readily soluble addition alloys are usually more effective; for example, calcium-manganese-silicon alloy has often been found to be more reliable and efficient than the more highly concentrated calcium-silicon alloy. Calcium, when used in conjunction with 0.10 to 0.20 per cent of aluminum, titanium or zirconium to produce inclusions of the peritectic type, provides a measure of safety by minimizing any tendency to low ductility caused by oxide galaxies. The ductility of steel of the peritectic type approaches closely that found in steel of the silicate type, and in addition the steel treated with larger amounts of strong deoxidizers is more resistant to hot tearing.

It is believed that the solidification diagrams represent broadly the mechanism by which the inclusions were formed. Interpretation of the appearance of inclusions by empirical reconstruction of the solidification mechanism, however, at best is only a substitute for quantitative equilibrium diagrams, but until such information is available diagrams of an empirical character appear to be useful. They must, however, be

applied with great care and can be utilized only to indicate trends, except under the exact condition used for construction of the diagrams.

#### ACKNOWLEDGMENTS

The authors desire to express their appreciation of the cooperation of the Staff of the Union Carbide and Carbon Research Laboratories, Inc. They wish particularly to acknowledge the encouragement and suggestions of J. H. Critchett, Vice President, and A. B. Kinzel, Chief Metallurgist, the assistance of C. O. Burgess, Research Metallurgist, in reading the manuscript, of D. N. Beregekoff in the preparation of metallographic specimens, and of H. M. Boos in making the steel. They also wish to thank J. S. Marsh, Physical Metallurgist, of the Alloys of Iron Research staff, for reviewing the solidification diagrams.

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#### DISCUSSION

(Harold K. Work presiding)

J. B. CAINE,\* Lockland, Ohio.—This subject is extremely important, and one in which definite proof on almost any point is conspicuous by its absence. Most of this proof is extremely difficult or impossible to obtain.

The type of inclusion shown in Fig. 14 can be found also in steels deoxidized with silicon aluminum. Fig. 16 shows inclusions of this type found in acid electric steel deoxidized with 0.08 per cent Al and 0.16 per cent Si as the final addition. These inclusions cannot be distinguished from the inclusions found in the same type of steel when 0.08 per cent Al and 0.10 per cent Ca, added as calcium-silicon, was used as the

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final deoxidizing addition, as shown in Fig. 17. For that matter, silicon-killed steels also show duplex sulphide inclusions (Fig. 18). The effect of these two final deoxidizers on the physical properties is also similar. The same improvement in ductility is obtained with the use of silicon aluminum as when calcium silicon aluminum is used as the final deoxidizing addition.

If this is true it would seem that it is necessary to differentiate between the effect of silicon and calcium silicon on the metal sulphide equilibrium. Would it not be



FIG. 16.—INCLUSIONS IN ACID ELECTRIC STEEL DEOXIDIZED WITH ALUMINUM AND SILICON.  $\times 500$ . UNETCHED.

FIG. 17.—SAME TYPE OF STEEL AS FIG. 16 DEOXIDIZED WITH ALUMINUM AND CALCIUM.  $\times 500$ . UNETCHED.

possible, if the addition of pure calcium to molten steel is impractical, to add the calcium as an alloy of some more inert metal, say nickel or copper?

It has been the writer's experience that the sequence and timing is very important when another element is added with aluminum. Were the calcium, zirconium, titanium and vanadium additions given in Table 5 added before, with, or after the aluminum addition, and if added before or after the aluminum, what was the approximate time interval between the aluminum addition and the other addition?

H. D. PHILLIPS,\* Lebanon, Pa.—The fact noted by the authors that certain inclusion forms exert a definite influence on hot tearing of steel castings is a confirmation of the experience of many practical steel foundrymen, as it has long been observed that in steels containing the intergranular sulphide form of ternary eutectic inclusion, the tendency to hot-tear is considerably increased over steels containing either the silicate or the alumina or peritectic type of inclusion. The findings of these authors differ from those of others only in that it has previously been observed that steels of the silicate type were more resistant than any of the others to hot tearing.

It has been the present writer's experience that for steels treated with high aluminum additions, between 0.10 and 0.15 per cent, the average physical properties for a large number of commercial heats of medium carbon steel of 0.04 per cent S were as follows: tensile strength, 72,500 lb. per sq. in.; yield strength, 41,750 lb. per sq. in.;

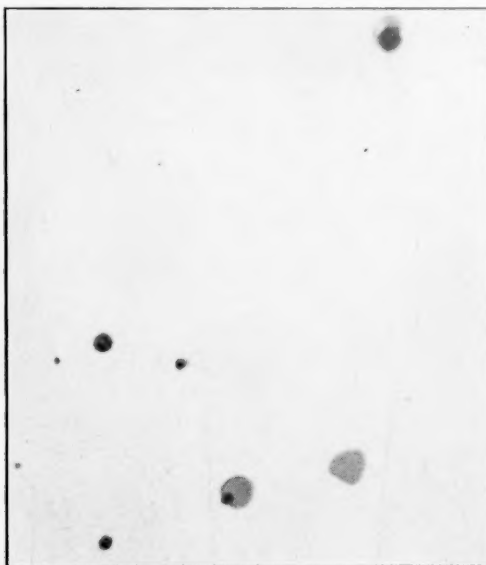


FIG. 18.—DUPLEX SULPHIDE INCLUSIONS IN SILICON-KILLED STEEL.  $\times 500$ . UNETCHED.

elongation, 30.5 per cent; reduction of area, 46.5 per cent. The bars were given a normalizing treatment with no tempering. None of the bars annealed and tempered after the normalizing but some were given a 400°F. temper and the average properties were as follows: tensile strength, 72,200 lb. per sq. in.; yield strength, 41,500 lb. per sq. in.; elongation, 31.0 per cent; reduction of area, 51.5 per cent.

An anneal between the normalize and temper probably would have improved these bars even more. The intention here is to show that properly made steels treated with high aluminum alone do show physical properties better than those quoted by the authors as taken from the work of Sims and Dahle.

The 400°F. temper has a very beneficial effect on the properties of steels treated with large amounts of strong deoxidizers. It would be interesting to know whether the authors' experiences check on this and, if so, their explanation of the improvement secured.

In a steel casting, which receives no advantage from mechanical working, inclusion form is a potent factor in the making of a consistently good, sound product and this work by the authors is welcome and extremely helpful.

\* Lebanon Steel Foundry.



C. W. BRIGGS, \* Cleveland, Ohio.—From my observations of commercial cast steels I feel that there might be some difficulty in trying to class, by the microscope alone, the inclusion type. It depends a great deal upon the field examined whether it is classified as galaxy or alumina type, for example. If the percentage of aluminum used is known, and the mechanical properties, a classification more in line with those of the authors could be made.

Foundrymen should guard against the sweeping statements that the authors have made concerning hot-tear formation. The information they present does not justify the inclusion of such statements in their conclusions. They have not presented any information as to the dimensions of their test piece, the manner in which it was produced or data obtained. In fact, they state that only a limited study was undertaken, and those of us who have studied this subject know that not even tentative conclusions can be based on limited information. The subject is much more complex than the authors indicate and the use of a certain type of deoxidizer is not going to make the steel "relatively resistant to hot-tearing."

R. H. FRANK, † Columbus, Ohio.—All steel foundrymen, whether they are willing to admit it or not, have had difficult times with hot-tearing which shows up at the most inopportune times. Much has been said and less has been written as to the cause, but more research work such as the authors have described will go a long way in the direction of a complete solution of the problem.

I do not believe that all of the so-called hot-tearing can be directly attributed to metal conditions—other factors must be taken into consideration, such as the resistance of the molds and cores to the natural shrinkage of the casting—but I do believe that the metal condition contributes to the larger percentage. It would be decidedly interesting to hear more details on just how the authors' tests were conducted, such as the composition of the sand used (whether green or dry), method of gating, heading and pouring, and how long the specimens were left in the sand before they were shaken out. I have examined a number of castings showing hot-tears—that is, from regular production, not experimentally—and have found that some show the intergranular eutectic type while others show the well rounded type scattered at random. All of the heats examined were deoxidized only with silicon and manganese and were under 0.40 per cent S. These irregularities can then be attributed to other causes, as mentioned above, but, as the authors say, it may be more advantageous to treat the steel with large amounts of strong deoxidizers, since they are more resistant to hot-tearing. In this manner then, at least a large percentage of the hot tearing will be eliminated.

We have tried numerous heats from 0.075 to 0.15 per cent Al, as suggested by Sims and Dahle, but have not been able to produce consistent results. We have always found some reduction in ductility, but some were so low that they would not pass on specification heats. Naturally then, we did not feel we could standardize on a practice that did not give consistent results. I was pleased to see that the authors, when discussing additions of 0.10 per cent Al, use the expression "under ideal conditions the inclusions consist of randomly distributed alumina." In commercial practice, it is not an easy matter to get "ideal conditions." In the next sentence, they say: "if the composition of the steel is unbalanced or the deoxidizing addition is not well diffused, the steel tends to contain either oxide galaxies or intergranular sulphides." I should like to ask the authors to explain their meaning of an "unbalanced composition" and a "deoxidizing addition that is not well diffused."

From our own observations, we are in hearty agreement with the authors that sulphur plays an important role in hot-tearing. It may differ in different practices, but

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in our acid electric practice, we concur with the authors in thinking that 0.040 S is a critical amount.

In their conclusions, the authors state that "the ductility of steel of the peritectic type approaches closely that found in steels of the silicate type and in addition the steel treated with large amounts of strong deoxidizers is *more resistant to hot-tearing*." That statement itself is, if it can be accomplished in commercial practice, worth considerable to the steel-casting industry.

G. F. COMSTOCK,\* Niagara Falls, N. Y.—This paper seems to present a new method of treatment of the subject, and the authors deserve credit for working out their theory in such a plausible manner. It may be questioned, however, whether they are justified in failing to correlate this new theory, based mainly on the idea of solubilities, with the older, or more familiar, theory based on the conception of relative deoxidizing power, or relative affinities of iron and the deoxidizing elements for oxygen.

For instance, it should be explained how the diagrams of Fig. 2 and Fig. 5 or Fig. 8 can be fitted in with the well-established stronger deoxidizing power of aluminum as compared with silicon. These diagrams seem to show that the oxide of Figs. 5 and 8, which may be alumina, is more soluble in the metal than the oxide of Fig. 2, which is silica. This would naturally imply that silicon and oxygen, existing together in the liquid steel, separate out at a higher temperature than that at which aluminum and oxygen, occurring in like manner, will separate, and is hard to reconcile with the well-known fact that aluminum will deoxidize silicates. The latter fact indeed seems to be an entirely sufficient explanation for the absence of typical silicates in aluminum-treated steel, and it would be interesting to know why the authors did not take it into consideration.

It is also a surprise to read that they consider oxide inclusions other than those of the "galaxy" type to be normally expected with the network or "eutectic" sulphides. In the writer's experience these two types characteristically occur together in commercial aluminum-treated cast steels, instead of being encountered together only "in some steels, probably owing to segregation," as stated in the paper.

It must be admitted that the occurrence of alumina, zirconia, and other refractory oxide inclusions in groups or "galaxies" is rather difficult to account for in a satisfactory manner, and the explanation based on the formation of a eutectic between the oxide and the metal is an interesting one and worthy of consideration. Other explanations must probably be based on an assumed pre-existing segregation of the oxygen in some form, possibly as a slag globule before the addition of aluminum. Such a globule might then be reduced largely to metal by the aluminum, leaving the aluminum oxide in fine solid particles which are not hot enough to coalesce. Surface-tension effects and simple refractoriness may account for the occurrence of alumina in particles that always remain comparatively small. The eutectic theory offered in this paper does not seem to be much more firmly established than the previous explanations, though it is presented in a skillful and impressive manner.

In discussing inclusions of the "alumina type," occurring when higher aluminum additions are used to restore a fair amount of ductility, the explanation seems to be based on oxide-sulphide ratios, rather than on the ratio of aluminum to oxide. Naturally, with lower sulphur, there is better ductility because less sulphide network can form. What needs to be explained is why, with the same sulphur and oxygen contents, more aluminum than is required merely for deoxidation gives less ternary sulphide eutectic of the intergranular type and therefore better ductility. A clearer explanation of this point on the basis of the authors' theory would make their theory more acceptable and useful.

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The information offered on the effect of calcium is interesting, as is also the theory of the peritectic reaction giving rise to duplex inclusions. In the writer's experience such duplex silicate inclusions have been found more often in titanium-killed steels than in steels deoxidized only with manganese and silicon, but no attempt has been made to explain this on the basis of a slag constitutional diagram as the authors have done in Fig. 14. Duplex inclusions, of course, are not unknown in the comparatively simple iron-silicate system.

G. SOLER,\* Canton, Ohio.—The authors' theory on the formation of inclusions in steel castings provides a working hypothesis for considering a number of problems related to deoxidation. It might be suggested that aluminum nitride inclusions may be present under the conditions of these experiments.

I would like to ask the authors if they would relate their theories of sulphide inclusions with hot shortness, which occurs in steels of high sulphur content. How could hot tearing be reduced by manipulating the deoxidizing elements such as aluminum and silicon in the making of fine-grained steels?

C. E. SIMS,† Columbus, Ohio.—The paper by Crafts, Egan and Forgeng is an endeavor to explain in a logical manner the mechanism of the formation of nonmetallic inclusions, based on the meager data at present available. Any attempt to increase our knowledge by the interpretation of data is to be commended. I wish to commend the authors especially, however, on the position of importance given to the sulphides. They have too long and too often been neglected or ignored, although probably they are the most important of the inclusions in the matter of affecting physical properties.

In view of the importance of obtaining correct interpretations, however, the following is offered as a counter argument to stimulate discussion. Data gathered in my own researches on inclusions differ to some extent from those referred to by the authors and have led to different interpretations. Most of these data have been presented in the first two papers referred to by the authors.

At the bottom of page 238 it is stated that glassy silicates persist with aluminum additions up to 0.025 per cent. Fig. 19 is of a silicon-deoxidized steel to which 0.015 per cent Al was added. There is a complete absence of glassy silicates, which is not uncommon unless the aluminum has all been oxidized by long holding.

In the second paragraph of page 241 it is said that "the reduction or elimination of a randomly distributed oxide (silicate) phase is presumably due to restriction of the metal-oxide miscibility gap." A simpler and more probable explanation is that it disappears because all silica has been reduced by the aluminum.

All steels to which aluminum has been added, regardless of the amount, contain small oxide inclusions, which presumably are alumina. These have a strong tendency to form in clusters like those shown in Figs. 4a and 7b. The authors regard these as eutectic formations, yet they show none of the characteristics of eutectics. They occur in steels containing eutectic sulphides but not in the same places. These oxides are situated with the primary steel crystals whereas the eutectic sulphides are necessarily in the grain boundaries. The size of the clusters and their distribution is extremely haphazard.

In order that alumina or any other oxide may be part of a eutectic, by definition it is necessary for it to be quite soluble in steel, so soluble that most of it is in solution at the time the lowest melting mother liquid starts to freeze. Whereas there is some circumstantial evidence to indicate a slight solubility in liquid steel for silica and alumina, no such solubility as would be necessary for eutectic formation has yet been shown. Assuming some solubility, however, it is still almost certain that the steel

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† Battelle Memorial Institute.

would be saturated at the time freezing starts and precipitation would take place throughout the range of solidification. This is not the condition for eutectic formation.

Fig. 10a shows "immiscible alumina." It is usual to find such small, black, globular inclusions in steels that have been treated with a large enough excess of aluminum, say 0.2 per cent. Fig. 20 shows such inclusions in a 0.25 per cent Al steel. They have been identified as  $\text{Al}_2\text{S}_3$ .

Steels tested with intermediate amounts of aluminum, say 0.05 per cent, usually show duplex sulphides such as are shown in Fig. 3. These are very similar to the duplex inclusions shown in Fig. 13a in a steel treated with calcium. Steels treated with zirconium show similar inclusions. The dark areas of the inclusions in the aluminum-deoxidized steels have been identified as  $\text{Al}_2\text{S}_3$  and in the zirconium steels as  $\text{ZrS}$ . It is at least possible that the dark portion in the calcium-treated steels is  $\text{CaS}$ .

With reference to the discussion of an aluminum oxysulphide compound (p. 248) Haglund, in his method for the purification of bauxite, showed that  $\text{Al}_2\text{S}_3$  will flux  $\text{Al}_2\text{O}_3$  and lower the melting point some  $500^\circ\text{C}$ . On solidification, however, the alumina separates as pure crystals.

On page 245, there is indicated to be a critical amount of sulphur in the neighborhood of 0.040 per cent. On the theory that the low ductility of some aluminum-deoxidized steels is due to eutectic sulphides that form broken envelopes around the primary grains and constitute zones of weakness, it is logical to assume that the more sulphide there is, the greater will be the effect. And that is exactly what the comparative data on a large number of heats of steel show. The relation is almost proportional to the sulphur content.

The sulphides in Figs. 4b and 4c undoubtedly are part of a eutectic, but it is difficult to subscribe to the idea that the sulphides of Figs. 1b, 7a, 10b, 13a and 13b are eutectic formations. Their position does have a pattern that roughly follows the grain boundaries, but the irregularities of their size, shape and spacing indicate that the sulphide has a limited solubility (lower than those in Figs. 4b and 4c), that saturation is reached when the steel is partly solidified, and that then the sulphides precipitate in the interdendritic channels.

If we take a broader view of the meaning of a eutectic, we might say they are part of a metal-sulphide eutectic in which the ratio of metal to sulphide is very high. I admit considerable uncertainty about the exact mode of formation, but would like to know.

W. CRAFTS, J. J. EGAN AND W. D. FORGENG (authors' reply).—In reply to Mr. Caine, it is possible that the duplex inclusions shown in his Figs. 16 and 17 are of a peritectic nature. It is believed, as was shown by Gagnebin, that elements other than calcium are capable of producing the peritectic condition, and it is also possible that calcium in the ferrosilicon may be responsible for these inclusions. Those shown by Mr. Caine in Fig. 18, containing a spherical oxide, are usually formed by lack of solubility of the oxide and sulphide components during cooling and are not considered to be formed by a peritectic reaction.

The matter of sequence and timing is of the greatest importance in the commercial manufacture of steels treated with large amounts of aluminum. The addition of calcium seems to improve this condition somewhat. In making laboratory heats, the order of addition has been found to be of less significance than the degree of diffusion of the deoxidizer, and the more dilute alloys have been found to be more effective; for example, calcium-manganese-silicon alloy has been found more effective than calcium-silicon alloy.

Mr. Phillips' comments on resistance to hot tearing are believed to confirm our results. The steels of the silicate type tend to shrink less and therefore are not sub-

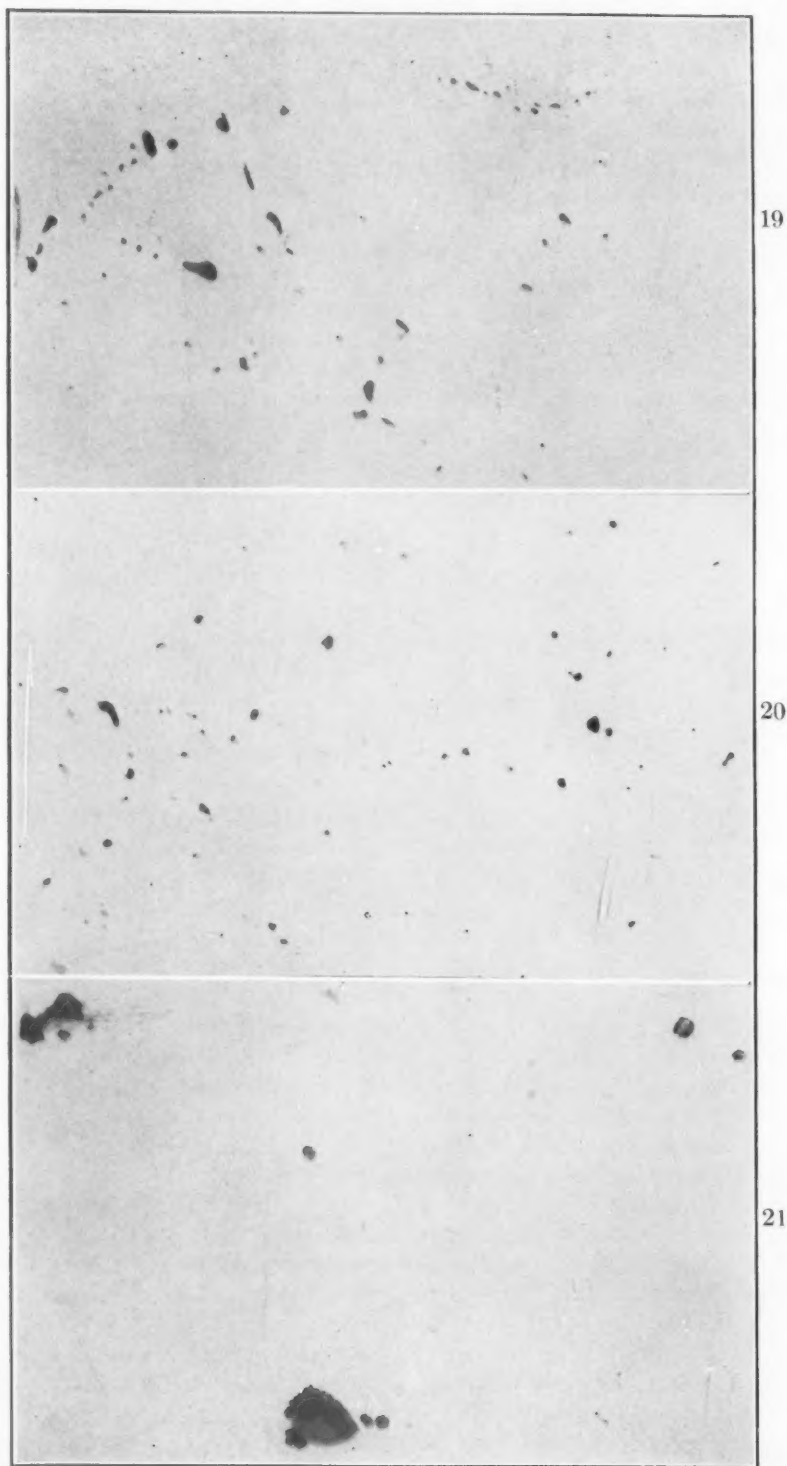


FIG. 19.—GRADE B CAST STEEL, UNETCHED,  $\times 250$ . 0.15 PER CENT ALUMINUM ADDED.  
FIG. 20.—GRADE B CAST STEEL, UNETCHED,  $\times 250$ . 0.25 PER CENT ALUMINUM ADDED.  
FIG. 21.—GRADE B CAST STEEL, UNETCHED,  $\times 1000$ . 0.05 PER CENT ALUMINUM ADDED.



jected to as great a strain as more highly deoxidized steel. The less strongly deoxidized silicate steels, however, are believed to be less resistant to tearing because of their tendency under oxidation to form the intergranular type of inclusions. The tensile properties of Mr. Phillips' 0.04 per cent S aluminum-treated steels are of a high order and represent excellent practice. They might be improved somewhat by the use of a calcium alloy. The low-temperature baking treatment undoubtedly improves ductility but the explanations so far offered do not seem to be well founded. Our experience does not confirm the popular belief that only steels of the high-aluminum type require the treatment. Silicate steels may also be benefited to a high degree.

Mr. Briggs' doubt that inclusions can be classified by use of the microscope emphasizes the need for care and thorough examination. The mechanism of solidification described in the paper has been reconstructed from the character and arrangement of inclusions, and great care was taken in classification of types and determination of their presence in many fields in each sample. This work was done at high magnification

after careful polishing, with the support of polarized light and etching reagents in doubtful cases.

The statements regarding hot tearing, which were questioned by several discussers, resulted from tests using the pattern shown in Fig. 22, which was made up in dry sand and poured through the gate at the small end. If cracking occurred it was at the junction of the heavy flange and the central bar. A section for microscopic examination was cut at that point and in some cases an intergranular film was found in steels that showed no obvious crack. In steels containing silicate inclusions the results were erratic, ranging as follows: (1) a crack that formed because the metal did not shrink properly but instead formed a sub-

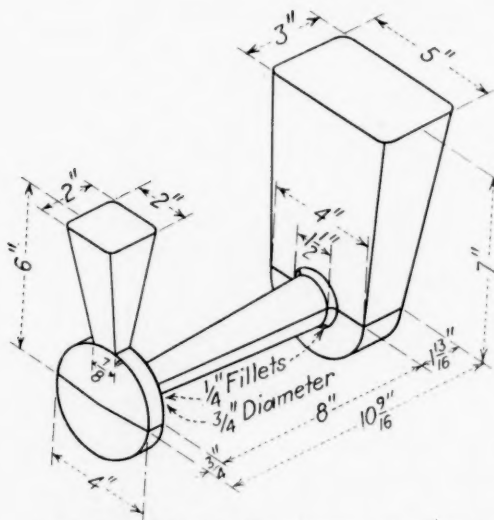


FIG. 22.—HOT-TEARING TEST CASTING.

surface blowhole at the place where the last metal solidified, (2) no tearing, and (3) an intergranular film or open crack. In steels treated with enough aluminum to produce intergranular inclusions, the castings had the crack or oxidized film consistently. When enough aluminum was added to eliminate the intergranular eutectic inclusions, either with or without calcium, no cracking or intergranular film was found. While these tests cannot be generalized too broadly, it is believed that they indicate that the more highly deoxidized steels are more resistant to hot-tearing.

Some of Mr. Frank's questions regarding hot-tearing have already been discussed, and it should be emphasized that no cure for hot-tearing has been advanced. The more highly deoxidized steels have not cracked in our tests and are believed to be less sensitive to cracking. They do tend to shrink more and are therefore unsuited to certain types of castings. It is believed that the steels that shrink less should be used in castings that cannot be fed properly, whereas the more deeply shrinking steels should be used where adequate feeding is possible. The hot cracking referred to in this paper should not be confused with the type of cracking that is in reality an external pipe or shrinkage cavity. Obviously, that type of defect will be increased by strong deoxidation, especially in light, poorly fed castings.

As mentioned above and by Mr. Caine, the time, sequence, and distribution of deoxidizing additions are very important. It is obvious that if a steel to which 0.10



per cent Al is added is not uniform in composition, the inclusions will vary in proportion to the concentration of deoxidizer. Thus unless the steel is made properly or the deoxidizing addition is uneconomically excessive, a wide variation in inclusion types may be produced.

Mr. Comstock's criticism that the mechanism of solidification has not been sufficiently correlated with the theory of deoxidation is justified. This was not undertaken because, in the first place, we lack the data to make it significant, and in the second place because knowledge of the compositions of the inclusions is not essential to reconstruction of the method by which they formed. Until the pertinent equilibrium diagrams are available it will not be possible to prove the mechanism of formation of the galaxy. The facts that the galaxy consists of two or three different nonmetallic components, that its tendency to segregate at the junctions of grains and at the ends of columnar crystals, its intensification at critical aluminum contents and its dependence on the oxygen-sulphur ratio, seem strong evidence of its eutectic nature. The latter is borne out by the following data on 0.30 per cent carbon steels made as described in the paper and treated as shown in Table 6.

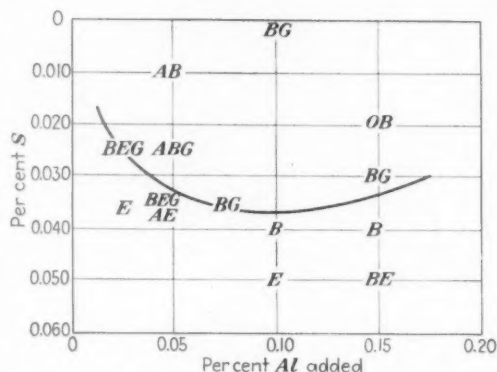


FIG. 23.—INCLUSIONS IN ALUMINUM-TREATED STEEL.

TABLE 6.—Data on 30 Per Cent Carbon Steels

Deoxidizing Additions, Per Cent				Inclusions <sup>a</sup>
Mn	S	Fe <sub>2</sub> O <sub>3</sub>	Al	
1.0	0.035		0.028	BE (G)
1.5	0.035		0.028	E
1.0	0.035		0.045	ABG
1.5	0.035		0.045	BEG
0.75	0.010		0.050	AB
1.5	0.035		0.050	AE
0.75	0.035		0.073	BG
0.75	0.010	0.63	0.10	BG
0.75	0.035		0.10	ABG
0.75	0.050		0.10	E
0.75	0.050	0.63	0.10	B
0.75	0.020		0.15	OB
0.75	0.030		0.15	BG
0.75	0.040		0.15	B
0.75	0.050		0.15	BE

<sup>a</sup> B indicates round sulphide; E, intergranular sulphide; G, galaxy; A, alumina; O, oxide; S, silicate.

If the oxide-sulphide ratio be plotted by evaluating an increase to 1.5 per cent Mn as equivalent to an increase of 0.010 per cent S, and an addition of iron oxide equivalent to a decrease of 0.010 per cent S, as shown in Fig. 23, the dependence of the galaxy on

a high oxide-sulphide ratio will be evident. The borderline mixture of both intergranular sulphide and oxide galaxy is also evident, and the limit of galaxy formation has been indicated. Similar data for zirconium-treated steels are given in Table 7.

TABLE 7.—Data on Zirconium-treated Steels

Deoxidizing Additions, Per Cent			Inclusions
Mn	S	Zr	
1.50	0.035	0.05	E
1.50	0.035	0.05	EBS
0.75	0.035	0.06	E
0.75	0.035	0.06	BE
0.75	0.035	0.12	BG
0.75	0.035	0.12	BG
0.75	0.060	0.12	BG
0.75	0.060	0.12	BG
0.75	0.020	0.15	BG
0.75	0.030	0.15	BG
0.75	0.040	0.15	BG
0.75	0.050	0.15	BG
0.75	0.060	0.15	B

As illustrated in Fig. 24, the range of the galaxy inclusions reaches a maximum at an appreciably higher sulphur content than in the aluminum-treated steels. These data are presented here in order to clear up a confusion that resulted from selection of ideal cases for illustration of the mechanism of solidification. It cannot be stated too strongly that these data represent only one closely controlled condition and that changes of composition and practice will produce major changes in the type of inclusions.

In order to correlate the observed inclusions with degree of deoxidation, Fig. 25 has been constructed to represent the effect of increasing silicon; increasing aluminum,

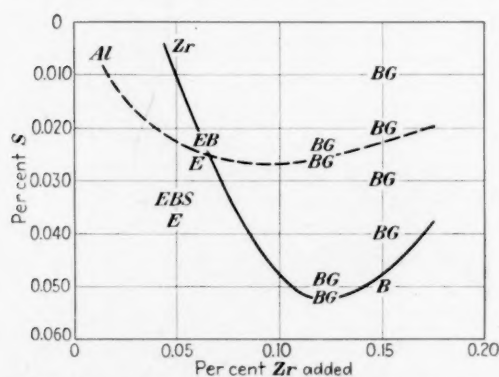


FIG. 24.—INCLUSIONS IN ZIRCONIUM-TREATED STEEL.

and/or sulphide inclusions with the larger aluminum additions is believed to lie in greater deoxidation and lack of solubility for the oxide, so that more oxide is separated with the metal and less is available for separation as an intercellular eutectic.

or zirconium in steel with 0.25 to 0.50 per cent Si; and increasing calcium in steel treated with 0.25 to 0.50 per cent Si and 0.10 to 0.20 per cent of aluminum or zirconium. The proportionate amount of the oxide types with respect to the sulphide types is also indicated. For comparison the relative ductility and resistance to hot tearing are also illustrated. The inclusion types that have been described in the ternary diagrams are indicated, except for the galaxy type, which is largely included in the range covered by the eutectic type. The reason for the decrease in the amount of ternary eutectic oxide

Dr. Soler's suggestion that nitrides be considered is pertinent. Nitride particles usually are associated with and may be an essential component of galaxies. There is a graduation in the size of galaxies, and nitrides usually are more prominent in the larger types. The very large galaxies are obviously more complex than is indicated in the paper, and the conditions surrounding their formation are not clear.

In regard to hot shortness of wrought steels it is believed that the hot tears in castings are comparable to ingot cracks but that secondary hot shortness as a result of oxidation during heating is not directly connected with the inclusion types. The use

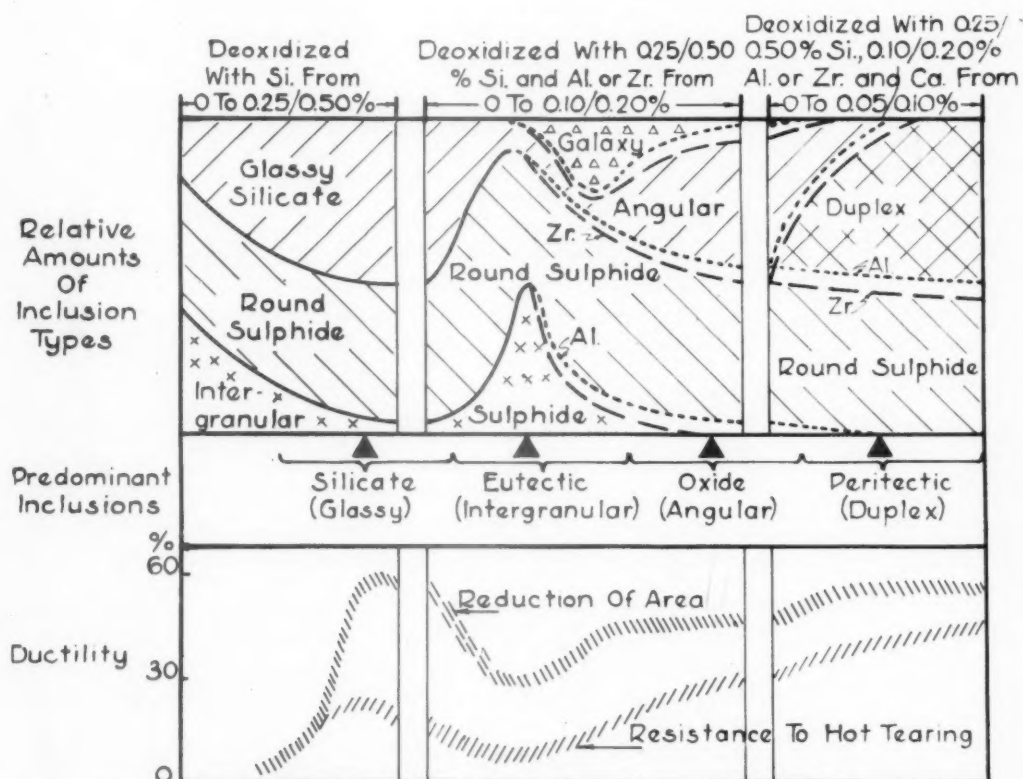


FIG. 25.—FIGURATIVE REPRESENTATION OF EFFECTS OF DEOXIDIZERS ON INCLUSIONS.

of zirconium in high-sulphur steel has been found helpful in wrought steel as well as in cast steel for reducing surface defects.

It is reasonable to believe that the inclusions shown in Mr. Sims' photomicrographs were produced under the conditions stated. Even more striking divergences from the conditions that we have considered to be typical might have been cited, and this emphasizes the qualitative nature of any inclusion study and the dependence of inclusions on oxide-sulphide ratio and other factors that enter into steelmaking. That similar inclusions can be produced under different conditions by different amounts of deoxidizer tends to confirm our theories of solidification.

We do not agree with Mr. Sims' statement that the galaxy inclusions have none of the characteristics of eutectics, but proof depends on the determination of the equilibrium diagrams. The statement that alumina cannot be sufficiently soluble in liquid steel to permit an oxide eutectic formation also awaits proof. Mr. Sims' description of the manner of separation of sulphides as a eutectic is in accord with our views.

Inclusions such as those shown in Fig. 10a and the central dark part of Fig. 13a are considered to be oxides and not sulphides. They have optical properties under plain and polarized light that usually are ascribed to oxides and they tend to disappear as the sulphur content is increased. The dark aluminum sulphide referred to by Sims and Dahle has not been encountered in this study, probably because of too low aluminum and sulphur contents, but a comparable zirconium sulphide having a tan color has been observed in high-zirconium steels.

In regard to the critical sulphur content and its effect on ductility, it is generally true that the higher the sulphur the lower the ductility. With certain ranges of sulphur below the critical amount, the oxide ternary eutectic galaxy is sometimes present and, although its presence does not seem to be as harmful as the intergranular sulphide, it often appears to be the reason for low ductility. Further, although low sulphur is desirable, there is an economical limit that seems to be just below the critical amount. In order to illustrate this, Table 8 gives the reduction of area of medium-carbon steels treated with 0.15 per cent of the indicated deoxidizer.

TABLE 8.—*Reduction of Area*

S, Per Cent	Reduction of Area, Per Cent with Deoxidizer Indicated	
	Al	Zr
0.020	45.2	46.9
0.030	44.0	46.9
0.035 (Ca)	44.9	42.2
0.040	39.4	36.0
0.050	38.5	39.7
0.050 (Ca)	48.6	52.0

The aluminum-treated steel has a critical content of somewhat less than 0.040 per cent S when aluminum is used alone. With calcium a higher sulphur content gives good values. Zirconium steel has a higher critical sulphur content. With calcium, higher ductility was obtained at 0.050 per cent S than at 0.035 per cent, probably because of inclusions that have a less harmful effect on ductility.

In summarizing this discussion, it is evident that the determination of whether the galaxy is a eutectic and the dependent questions of the peritectic and the oxysulphide compound must wait for more quantitative corroboration. For the present the observed appearance as well as the corrective measures necessary to avoid the galaxy indicate in our opinion that it is a eutectic. The end point in the solidification of a metal-oxide-sulphide system is a eutectic implying a certain degree of solubility of the nonmetallic phases. This is obvious, and recognition of the amount and kind of eutectic or intercellular material is the key to ductility in steel castings. The problem of hot cracking does not appear to be simple but certain tendencies have been noted that are significant. In addition to its use as a guide toward control of inclusions and ductility in steel castings, it is hoped that this paper may stimulate study of the pertinent nonmetallic systems, as more accurate knowledge is necessary for inclusion control in all steel products.

## Heat Capacity of Iron Carbide from 68° to 298° K. and the Thermodynamic Properties of Iron Carbide

BY HARRY SELTZ,\* HUGH J. McDONALD,† AND CYRIL WELLS,‡ MEMBER A.I.M.E.

(New York Meeting, February 1940)

SEVERAL investigators have measured the heat capacity of cementite, using different methods of attack, but the agreement between the values obtained cannot be considered good. Naeser<sup>1</sup> has made measurements of "average heat capacities" of iron carbide between 1026° and 85° K., using a water calorimeter. His computed true specific heat at 78.1° K. is 11.22 cal. per gram-formula mass, which, if correct, is much too high for any reasonably accurate extrapolation to 0° K. The cementite used by Naeser was obtained from a steel containing 0.9 per cent carbon, by electrolytically dissolving out the iron in a neutral bath of ferrous chloride. The cementite remained as a coarse, crystalline, gray powder. Andes<sup>2</sup> has measured the specific heat of iron carbide, from 102° to 323° K., as it exists in steel. The specific heats of several slugs of steel of known iron carbide content were determined, and the specific heat of the iron carbide ( $\text{Fe}_3\text{C}$ ) calculated by plotting specific heat versus percentage of carbon, and extrapolating to pure  $\text{Fe}_3\text{C}$  (6.7 per cent C). The heat-capacity values for temperatures below 100° K. were obtained by comparing the temperature-specific heat curve for  $\text{Fe}_3\text{C}$  to that of Fe. Since the two were very similar in the range examined experimentally and approach more closely at low temperatures, it was assumed that near the absolute zero the form of the curve for  $\text{Fe}_3\text{C}$  would be similar to that of Fe. Andes calculates for the entropy of  $\text{Fe}_3\text{C}$ ,  $S_{298} = 23.55$  e.u.

The heat of formation of  $\text{Fe}_3\text{C}$  has been studied by several workers. Kelley<sup>3</sup> has reviewed these measurements and calculations, and selects those of Roth<sup>4</sup> and Naeser<sup>5</sup> as worthy of most consideration. Roth has given  $\Delta H = 5400$  cal.  $\pm 30$  per cent as a result of his own and other work. Naeser has determined the heat of formation from Fe and different forms of carbon, and for graphite ( $\beta$ ) he finds  $\Delta H = 5600$  cal. Kelley accepts the rounded figure  $\Delta H = 5500$  as the heat of formation at 298.1° K., but this value is quite uncertain.

Manuscript received at the office of the Institute Sept. 1, 1939. Issued as T.P. 1137 in METALS TECHNOLOGY, December 1939.

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<sup>1</sup> References are at the end of the paper.



To determine the free energy of formation of  $\text{Fe}_3\text{C}$ , Kelley<sup>3</sup> uses the available equilibrium data for the reactions  $3\text{Fe} + \text{CH}_4 = \text{Fe}_3\text{C} + 2\text{H}_2$  and  $3\text{Fe} + 2\text{CO} = \text{Fe}_3\text{C} + \text{CO}_2$ . From the first reaction, there is calculated  $\Delta F_{298.1} = 4450$  and from the second,  $\Delta F_{298.1} = 4770$ , and he adopts the mean value  $\Delta F_{298.1} = 4610$  cal. From the relationship  $\Delta F = \Delta H - T\Delta S$ , it is found for the entropy of formation,  $\Delta S_{298.1} = 2.99$ . This figure and the entropies<sup>6</sup> of iron and graphite result in  $S_{298.1} = 23.8$  for  $\text{Fe}_3\text{C}(\alpha)$ . Schenck<sup>7</sup> has studied also the equilibrium in the reaction,  $3\text{Fe} + \text{CH}_4 = \text{Fe}_3\text{C} + 2\text{H}_2$ . His data are scattered and do not permit definite calculations, therefore Kelley had selected the work of Watase<sup>8</sup> on the same reaction in arriving at the free energy of formation of  $\text{Fe}_3\text{C}$ . Schenck's data have been considered, however, by Yap and Liu.<sup>9</sup> From his data they computed the heat of formation,  $\Delta H_{298.1} = 12,280$  and entropy,  $S_{298.1} = 31.8$  for iron carbide.

Schwarz and Ulich<sup>10</sup> have examined the low-temperature measurements of the heat capacity of  $\text{Fe}_3\text{C}$  made by Naeser. They believe his values below  $150^\circ \text{K}$ . are somewhat high, but that the curve below this temperature can be represented by expression  $C_p = 4D\left(\frac{490}{T}\right)$ ; that is, by four similar Debye functions with a  $\theta$  value of 490. This value of  $\theta$  was arrived at by considering the  $\theta$  values for iron (420) and graphite (2000). On the basis of this extrapolation they arrive at the value  $S_{298.1} = 23.9$  e.u. for  $\text{Fe}_3\text{C}$ . Kelley<sup>6</sup> also has considered Naeser's low-temperature measurements and by applying the  $n$ -formula of Lewis and Gibson<sup>11</sup> for the purpose of extrapolation finds  $S_{298.1} = 32.8$  e.u., of which 8.64 is extrapolation below  $70.8^\circ \text{K}$ . He believes that the error in this value may be several units, and does not recommend its use.

An examination of these different values for the entropy of  $\text{Fe}_3\text{C}$  shows that they may be divided into two groups; one set of values ranges between 30 and 32, while the other set ranges between 23 and 25. It seemed that a further investigation of the specific heat of iron carbide at low temperatures might allow one to choose the best value for the entropy.

#### PREPARATION OF IRON CARBIDE

Carbonyl iron that had been examined spectroscopically was selected as most suitable for the preparation of high-purity iron by further hydrogen purification. The impurities present in largest amounts in this iron as received are oxygen and carbon and these were removed by heating in hydrogen for 500 hr. at  $1200^\circ \text{C}$ . The iron content of the material thus purified was probably better than 99.95 per cent. Carbonyl iron that was similarly treated has been analyzed completely and the results are given elsewhere.<sup>12</sup> The carbon used in the preparation of the iron-carbon alloy was obtained from chemically pure benzene vapors passed through a heated Armeo iron tube, where the carbon from the decomposition deposited out.

Weighed amounts of iron and carbon (enough to give a content of carbon of about 1.5 per cent) were placed in a crucible of chemically pure magnesium oxide and melted in an induction furnace. The magnesia crucible was contained in a graphite crucible which at the high temperature of the induction furnace maintained a reducing atmosphere. The mixture was heated to above the melting point in about 3 hr. and was held at this temperature for  $\frac{1}{2}$  hr. and allowed to cool to  $1000^{\circ}\text{C}$ . in another  $\frac{1}{2}$  hr. The alloy was then slowly cooled to room temperature.

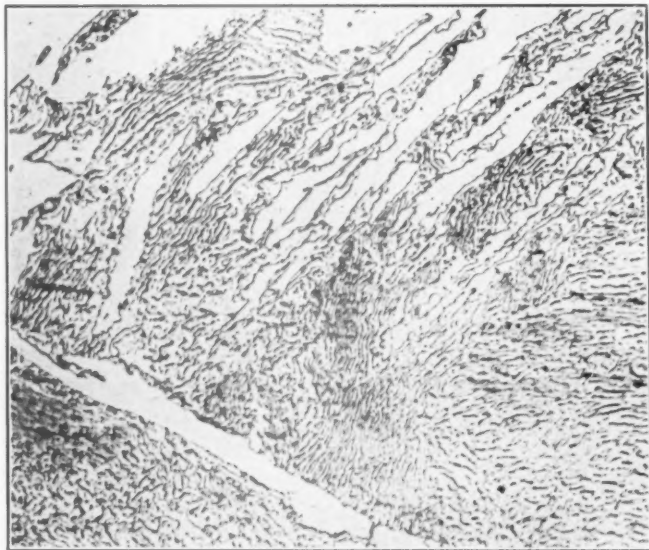


FIG. 1.—ALLOY CONTAINING 1.35 PER CENT C.  $\times 300$ .

Ingot slowly cooled. Etched with Nital. Shows evidence of proeutectoid cementite (white) with pearlite and absence of graphite.

Microscopic examination of the ingot, Fig. 1, showed proeutectoid cementite and pearlite, but did not reveal any graphite. Carbon analyses, which were run in duplicate on five representative samples of the ingot, gave 1.354 per cent as the average carbon content. This figure was used in calculating the percentage of iron carbide in the steel, the solubility of carbon in  $\alpha$  iron being neglected since at room temperature it is probably less than 0.01 per cent.<sup>13</sup> The steel sample was sawed into small pieces and packed in the calorimeter. The weight of the sample, in vacuo, was 179.791 grams and thus contained 0.20294 mol of  $\text{Fe}_3\text{C}$  and 2.5673 mols of iron.

#### APPARATUS

The calorimeter used in these measurements was modeled after that described by Gibson and Giauque,<sup>14</sup> and since no significant modifications were made, it will not be described further. The calibrations of the calorimeter and shield windings were made by comparison with copper-constantan couples previously checked against a standardized couple, S6, which was made available through the kindness of Prof. J. G. Aston,

of Pennsylvania State College. This couple had been calibrated in terms of a helium thermometer.<sup>15</sup> The measurements of specific heat were carried out as described by Gibson and Giauque<sup>14</sup> and the usual corrections for heat interchange between the shield and calorimeter were made. The free space in the calorimeter was filled with hydrogen during the measurements and rapid distribution of heat was achieved as indicated by a negligible temperature lag after introduction of the electrical energy. The over-all accuracy of the measurements of the total heat capacities of the sample ( $\text{Fe} + \text{Fe}_3\text{C}$ ) is believed to be  $\pm 0.4$  per cent.

TABLE 1.—*Experimental Results*

Run 1		Run 2		Run 3	
$T^\circ \text{ K.}$	Experimental $C_p$ Calorimeter plus Steel Sample	$T^\circ \text{ K.}$	Experimental $C_p$ Calorimeter plus Steel Sample	$T^\circ \text{ K.}$	Experimental $C_p$ Calorimeter plus Steel Sample
197.77	22.75	81.28	10.21	68.00	8.02
201.54	23.08	85.10	10.93	71.30	8.54
205.36	23.24	88.98	11.64	75.43	9.16
207.15	23.27	93.02	12.42	79.62	9.90
210.95	23.52	100.75	13.71	83.80	10.61
214.65	23.65	104.70	14.25	87.80	11.31
218.10	24.00	108.90	14.70	101.11	13.72
225.89	24.12	112.73	15.15	113.75	15.38
229.67	24.42	120.20	16.00	122.84	16.39
233.22	24.44	129.75	17.05	134.25	17.72
243.15	24.88	139.00	18.21	144.55	18.70
253.30	25.35	148.68	19.07		
263.30	25.66	157.00	19.85		
269.27	25.88	167.11	20.68		
273.13	25.89	177.90	21.44		
277.02	26.07	188.75	22.17		
280.36	26.22	197.46	22.71		
284.30	26.24	208.21	23.37		
288.10	26.40	218.70	23.84		
292.06	26.61	228.25	24.36		
295.30	26.66	239.50	24.73		
		250.31	25.20		
		261.36	25.59		
		273.31	25.94		
		284.30	26.26		
		296.70	26.66		

## EXPERIMENTAL RESULTS

In Table 1 the experimental results are tabulated. In the three runs the total measured heat capacities of calorimeter plus sample are given. The conversion from electrical energy to defined calories was made on the basis of 1 calorie = 4.1833 international joules.

From a smoothed plot of these data, Fig. 2, using the previously determined heat capacities of the empty calorimeter and the heat capaci-

ties of iron obtained by Simon and Swain,<sup>16</sup> the molal heat capacities of  $\text{Fe}_3\text{C}$  have been calculated at even temperature intervals (Table 2).

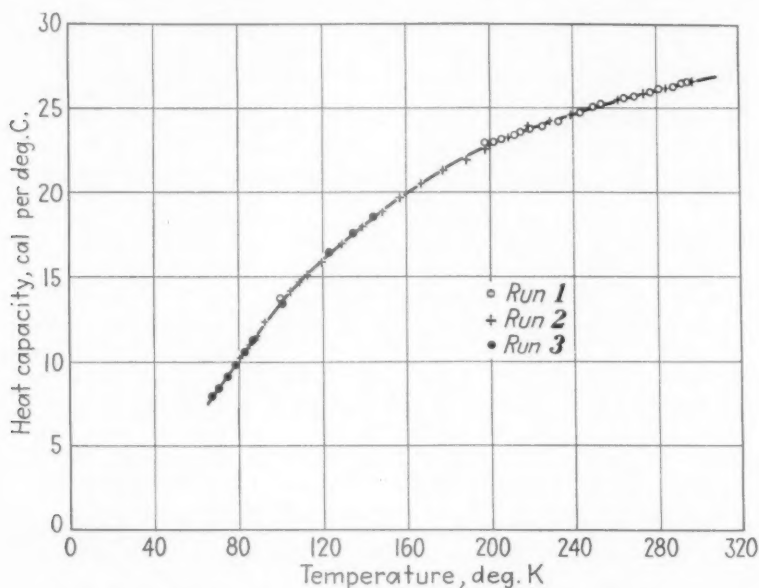


FIG. 2.—HEAT CAPACITY OF CALORIMETER PLUS SAMPLE.

It has been stated that the accuracy of the heat-capacity measurements of the total steel sample is estimated to be  $\pm 0.4$  per cent, but since this

TABLE 2.—Molal Heat Capacities of Iron Carbide

$T^\circ \text{ K.}$	Molal $C_p$	$T^\circ \text{ K.}$	Molal $C_p$
68	6.41	170	18.48
75	7.29	180	19.51
80	7.99	190	20.35
85	8.53	200	21.04
90	9.22	210	21.68
95	9.86	220	22.47
100	10.50	230	23.01
105	10.95	240	23.65
110	11.58	250	24.15
120	12.58	260	24.64
130	13.45	270	24.88
140	14.63	280	25.13
150	15.92	290	25.23
160	17.25	298.1	25.33

contained only 0.20294 mol of  $\text{Fe}_3\text{C}$  the over-all accuracy of the molal heat capacities for the carbide is probably not better than  $\pm 2$  per cent.

These values are plotted in Fig. 3 along with those reported by Naeser and by Andes, and it is seen that this investigation gives a heat-capacity curve that lies above theirs from  $150^\circ$  to  $290^\circ \text{ K.}$ ; at lower

temperatures it is below Naeser's and almost coincides with Andes'. Above 298° K. our values run fairly smoothly into Naeser's curve.

#### CALCULATION OF THE ENTROPY OF IRON CARBIDE

The entropy change of iron carbide from 68° to 298.1° K. was calculated in the usual manner by graphical integration of the curve  $C_p$  versus  $\ln T$  between these temperature limits. The value obtained was 23.16 e.u. For the extrapolation of the entropy from 68° to 0° K. it was found that the relation  $C_v = 3D\left(\frac{360}{T}\right) + D\left(\frac{1000}{T}\right)$  fitted the heat-capacity values within the experimental error from 68° to 130° K., as shown in Fig. 3. It is apparent also that the extrapolation to lower temperatures

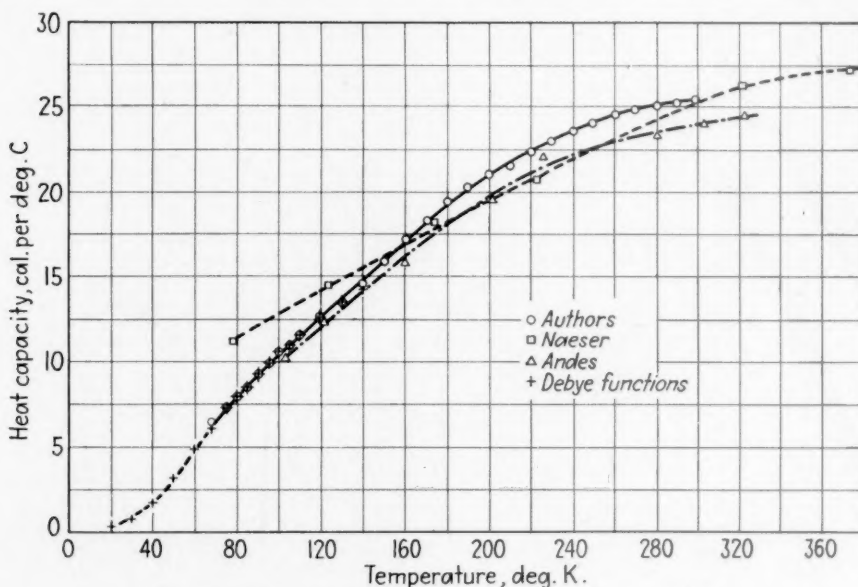


FIG. 3.—MOLAL HEAT CAPACITY OF IRON CARBIDE.

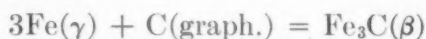
fits smoothly onto the experimental curve. The formulation of the heat capacity in terms of three equal Debye functions ( $\theta = 360$ ) and one Debye ( $\theta = 1000$ ) is not unreasonable, since the three equal Debyes can be associated with the lattice vibrations of three gram atoms of iron and the other accounts for the interpenetrating carbon lattice.<sup>17</sup> Using these values the entropy contribution from 0° to 68° K. is found to be 2.57 e.u., which gives for the total rounded entropy of  $\text{Fe}_3\text{C}$  at 298.1,  $S_{298.1} = 25.7$  e.u., which lies between the extreme values previously reported. The accuracy of this value is estimated to be within  $\pm 1$  e.u.

#### CALCULATION OF THE HEAT AND FREE ENERGY OF FORMATION OF IRON CARBIDE

For the reaction  $3\text{Fe}(\alpha) + \text{C}(\text{graph.}) = \text{Fe}_3\text{C}(\alpha)$  Kelley<sup>3</sup> accepts for the heat of formation  $\Delta H_{298.1} = 5500$  cal., and from equilibrium



studies at higher temperatures calculates the free energy of formation,  $\Delta F^\circ_{298.1} = 4610$  cal. From these values and the relation  $\Delta F^\circ = \Delta H - T\Delta S$  the entropy change is found to be  $\Delta S_{298.1} = 2.99$  e.u., and the entropy of  $\text{Fe}_3\text{C}$ ,  $S_{298.1} = 23.8$  e.u. This is 1.9 e.u. lower than that found in this investigation, 25.7 e.u. Furthermore, from data on heat capacity and heat of transition at higher temperatures, Kelley calculates that the free energy change for the reaction



passes through zero at  $1480^\circ \text{K.}$ , or, in other words, that the carbide is stable *relative to Fe( $\gamma$ ) and graphite* above this temperature and unstable below. This, as will be shown, is  $400^\circ$  higher than the temperature calculated from the experimental solubility curves for  $\text{Fe}_3\text{C}$  and graphite in austenite as determined by Wells.<sup>18</sup> With these discrepancies in mind, it was considered advisable to present the calculations from Wells' data and to compare the results obtained with Kelley's results and with the entropy of  $\text{Fe}_3\text{C}$  from this investigation.

From the stable solubility curve of graphite in austenite and the metastable solubility curve of  $\text{Fe}_3\text{C}(\beta)$  in austenite the corresponding percentages of carbon at several temperatures have been obtained. These values are given in Table 3, where  $P_g$  is the percentage of carbon in austenite that is in equilibrium with graphite, and  $P_\beta$  is the percentage of carbon in austenite that is in metastable equilibrium with  $\text{Fe}_3\text{C}(\beta)$ .  $N_\gamma$  is the mol fraction of  $\text{Fe}(\gamma)$  corresponding to  $P_\beta$ . We can then express the standard free-energy change for the reaction at any temperature:

$$\begin{aligned} \text{C}(\% \text{ in austenite}) &= \text{C}(\text{graph.}) \\ \Delta F^\circ &= -RT \ln \frac{1}{f \times P_g} = RT \ln P_g + RT \ln f \end{aligned}$$

and for the reaction:

$$\begin{aligned} 3\text{Fe}(\gamma) + \text{C}(\% \text{ in austenite}) &= \text{Fe}_3\text{C}(\beta) \\ \Delta F^\circ &= -RT \ln \frac{1}{N_\gamma^3 \times f_1 \times P_\beta} = RT \ln (N_\gamma^3 \times P_\beta) + RT \ln f_1 \end{aligned}$$

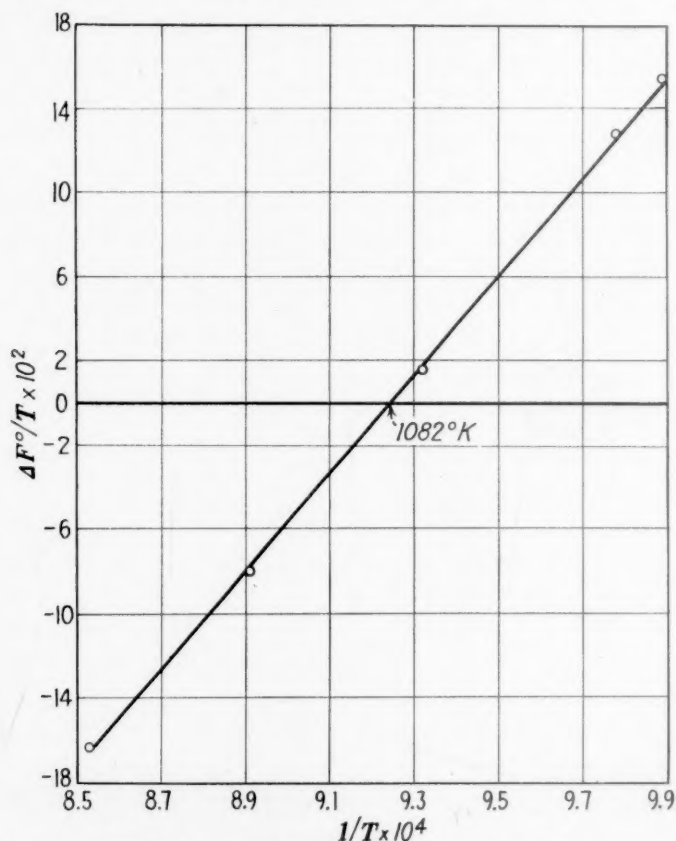
In these equations  $f \times P_g$  is the thermodynamic activity of carbon in austenite in equilibrium with graphite and  $f_1 \times P_\beta$  is the activity in equilibrium with  $\text{Fe}_3\text{C}(\beta)$ . The corresponding activity coefficients are  $f$  and  $f_1$ , and since the spread between the two solubility curves is never greater than 0.15 per cent carbon they can be considered equal. The activity of  $\text{Fe}(\gamma)$  is taken equal to its mol fraction, without appreciable error. Subtracting the first equation from the second gives:

$$\begin{aligned} 3\text{Fe}(\gamma) + \text{C}(\text{graph.}) &= \text{Fe}_3\text{C}(\beta) \\ \Delta F^\circ &= RT \ln \frac{N_\gamma^3 \times P_\beta}{P_g} + RT \ln \frac{f_1}{f} = RT \ln \frac{N_\gamma^3 \times P_\beta}{P_g} \end{aligned}$$

TABLE 3.—*Equilibrium Data*

Temperature, Deg. K.	$P_\alpha$	$P_\beta$	$N_\gamma$	$\Delta F^\circ$	$\Delta F^\circ/T \times 10^2$	$1/T \times 10^4$
1011	0.688	0.834	0.9625	156.6	15.49	9.89
1023	0.718	0.863	0.9611	132.1	12.91	9.78
1073	0.850	0.981	0.9560	17.8	1.66	9.32
1123	0.984	1.100	0.9508	- 89.5	- 7.79	8.91
1173	1.119	1.219	0.9457	-191.2	-16.30	8.53

since  $\ln \frac{f_1}{f} = 0$ . In column 5 of Table 3 the  $\Delta F^\circ$  values calculated from this equation are listed. Wells estimates an accuracy of  $\pm 0.005$  per cent

FIG. 4.—PLOT OF  $\Delta F^\circ/T$  AGAINST  $1/T$ .

for the solubility curves, which would mean an uncertainty of about  $\pm 15$  cal. in the  $\Delta F^\circ$  values. A plot of  $\Delta F^\circ/T$  against  $1/T$  is given in Fig. 4, which shows that the points lie satisfactorily on a straight line. From

the thermodynamic relation  $\frac{\delta\left(\frac{\Delta F^\circ}{T}\right)}{\delta\left(\frac{1}{T}\right)} = \Delta H$ , we calculate, from the

slope of the curve,  $\Delta H_{1082} = 2400$  cal., assuming that the heat of reac-

tion is constant for this short temperature range of 160°. A plot of the  $\Sigma$  function, taking into account the  $\Delta C_p$  values, gave  $\Delta H_{1082}$  within 50 cal. of this value. We estimate the accuracy of this value at  $\pm 100$  cal. From Fig. 4 it is found that  $\Delta F^\circ$  passes through zero at 1082° K., which means that, *relative to pure Fe( $\gamma$ ) and graphite*,  $\text{Fe}_3\text{C}(\beta)$  is stable above 1082° K., and metastable below this temperature. This is the reaction for which Kelley calculates a corresponding temperature of 1480° K. (p. 45 of ref. 3). On the other hand, for the reaction:

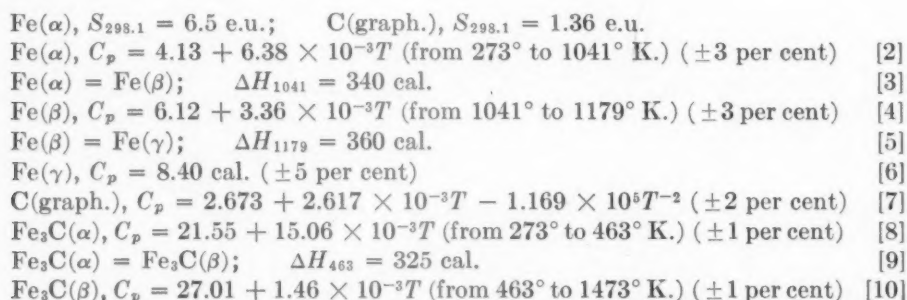


the free-energy change is negative up to the temperature where the extrapolated solubility curves of Wells intersect at 1473° K. In other words, below this temperature  $\text{Fe}_3\text{C}$  can still *decompose to give austenite, saturated with carbon, and free graphite*.

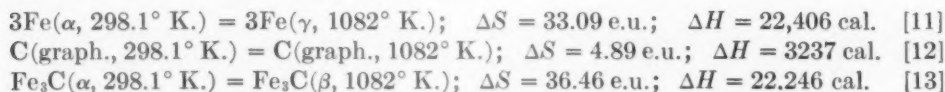
Accepting 1082° K. as the temperature at which  $\Delta F^\circ$  passes through zero, we write:



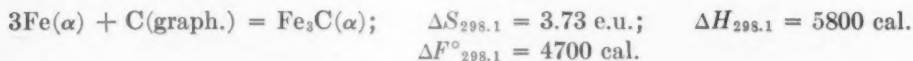
The value of  $\Delta S$  is calculated from the relation  $\Delta F^\circ = \Delta H - T\Delta S$ . From these data and heat capacities and heats of transition of iron, carbon and  $\text{Fe}_3\text{C}$  the thermodynamic quantities for the formation of the carbide at 298.1° K. can be calculated. The necessary thermal data are taken from Kelley's<sup>3,6,19</sup> publications:



From equations 2 to 10 we calculate:



Combining equation 1 with equations 11, 12 and 13 we obtain:



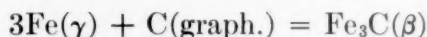
From this value of  $\Delta S_{298.1}$ , the rounded entropy of  $\text{Fe}_3\text{C}(\alpha)$  is  $S_{298.1} = 24.7$  e.u. compared with the value of 25.7 from our measurements. This is excellent agreement when it is considered that our value was obtained from heat-capacity measurements at low temperatures, and

this value was calculated from solubility measurements in the neighborhood of 1000° K. Comparing these figures with those given by Kelley, it is observed that  $\Delta H$  is greater by 300 cal. and  $\Delta F^\circ$  by about 100 cal. These differences are sufficient to explain the discrepancy in the temperatures at which  $\text{Fe}_3\text{C}(\beta)$  becomes stable, since the  $\Delta F^\circ$  values in this region are changing only slowly.

#### SUMMARY

1. The heat capacities of iron carbide,  $\text{Fe}_3\text{C}$ , have been experimentally determined from 68° to 298.1° K., and, using four Debye functions,  $3D\left(\frac{360}{T}\right) + D\left(\frac{1000}{T}\right)$ , for extrapolation, the entropy has been calculated;  $S_{298.1} = 25.7 (\pm 1)$  e.u.

2. From the solubility curves of Wells for carbon and  $\text{Fe}_3\text{C}(\beta)$  in austenite the free energy and heat of formation of the carbide have been evaluated. At 298.1° K. it has been calculated that  $\Delta H = 5800$  cal.,  $\Delta F^\circ = 4700$  cal. for the formation of  $\text{Fe}_3\text{C}(\alpha)$  and the entropy is found,  $S_{298.1} = 24.7$  e.u., within the limits of accuracy of the value given above. The temperature at which  $\Delta F^\circ$  becomes zero for the reaction:



is fixed at 1082° K.

#### ACKNOWLEDGMENT

The authors wish to thank Dr. V. N. Krivobok, Professor of Metallurgy, Carnegie Institute of Technology, who had the determinations of carbon in the steel carried out under his direction, and Miss E. B. Pearsall, of the Metals Research Laboratory, for the preparation of the photomicrographs of the sample.

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## DISCUSSION

(J. B. Austin presiding)

J. CHIPMAN,\* Cambridge, Mass.—This determination of the entropy of  $\text{Fe}_3\text{C}$  is probably, as the authors say, reliable to  $\pm 1$  e.u. However, the degree to which the results can be depended upon would have been improved by simultaneous measurements on pure iron. It should be noted that the heat capacity of  $\text{Fe}_3\text{C}$  as recorded is the difference between two larger quantities, and for this reason the method is peculiarly susceptible to experimental errors.

The authors have calculated from their data and Wells' solubility line the thermodynamic properties of  $\text{Fe}_3\text{C}$ . The results unquestionably are more accurate and more certain than earlier data.

The reader must be careful not to infer that  $\text{Fe}_3\text{C}$  becomes a stable phase of the iron-carbon system above  $1082^\circ\text{K}$ . It merely becomes more stable than graphite plus pure iron, not nearly so stable as graphite plus saturated austenite. Have the authors used their new data to calculate a temperature (perhaps hypothetical) at which cementite actually becomes the more stable phase? As I recall, the lines determined by Wells appeared to intersect at about  $1200^\circ\text{C}$ . Do the new data indicate a higher or lower intersection?

G. PHRAGMÉN,† Stockholm, Sweden.—The stability of iron carbide has been subject to discussion from the time when the first phase diagram of the iron-carbon alloys was drawn. Roozeboom assumed the carbide to be stable at temperature below  $1000^\circ\text{C}$ , but this idea was soon given up when it was found that the carbide might decompose and graphite form in this range of temperature. Several metallurgists, however, hold the view that the carbide is stable at high temperatures.

Some of them seem still to adhere to the assumption by P. Goerens in 1907, that graphite never does crystallize directly from the liquid alloy. Goerens himself abandoned this idea long ago.<sup>20</sup> From the microstructure of gray cast iron it is obvious that actually graphite crystallizes during the solidification, if the rate of cooling is not too rapid.<sup>21</sup> The metastability of iron carbide in gray cast iron at all temperatures below the eutectic must be accepted.

Gray cast iron has a considerable content of silicon. It is conceivable that the effect of the silicon is chiefly catalytic, the number of graphite nuclei or the rate of crystallization of graphite being increased. But the possibility of an actual change in the stability relations should also be considered.

The iron carbide is metastable if its carbon activity exceeds that of the graphite, both activities being referred to the same standard; for instance, the pure graphite. If the silicon, or some other "graphitizing" substance added, should dissolve measurably in the graphite, its carbon activity would decrease and thereby the carbide might

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<sup>20</sup> Compare Einführung in die Metallographie, Ed. 3, 231. 1922.

<sup>21</sup> See, for instance, Hanemann and Schrader: Atlas Metallographicus, 2, Fig. 165.



be caused to decompose or not to form. It is, however, rather improbable that such a solution would form.

The radius of the carbon atom is approximately  $0.8 \times 10^{-8}$  cm. whereas the radii of the silicon and iron atoms are approximately  $1.2 \times 10^{-8}$  cm. As a rule the formation of a solid solution by substitution is possible only if the atomic radii are not very different, and the formation of a solution of the interstitial type only if the atomic radius of the solute is small in relation to that of the solvent.

There is another, more probable way by which an additional substance may change the stability of the carbide.<sup>22</sup> The carbon activity of the iron carbide is indeterminate if the iron activity is not specified, because of the equation

$$\{\text{Fe}\}^3\{\text{C}\} = f(T)\{\text{Fe}_3\text{C}\}$$

the activities being denoted by  $\{\text{Fe}\}$ ,  $\{\text{C}\}$  and  $\{\text{Fe}_3\text{C}\}$ . Of course, the iron and carbon activities depend on the composition of the carbide, but the variation of the carbon content of the carbide is extremely small, and the activities cannot be calculated on this basis. If the iron activity is referred to pure iron as standard it has the same value in the carbide as in the iron phase that is in equilibrium with the carbide; i.e., if the substance added dissolves in the iron phase but not in the carbide, the iron activity will decrease and the carbon activity increase, provided that the carbon solubility is not reduced too much.

It is true that little is known about the distribution, between the three phases mentioned, of such graphitizing substances as silicon, aluminum, copper, nickel and cobalt. It seems plausible, however, that they dissolve in the iron phase and not in the carbide or in the graphite. It might be added that the effect of a certain percentage seems to be smaller when the atomic weight is higher (see, for instance, Seventh Report on the Heterogeneity of Steel Ingots, Iron and Steel Inst. 191, 1937) as it should be according to the theory mentioned. Also, this theory implies that the graphitization will proceed more easily within the iron phase or at the interface between the iron and the carbide than within the later phase; if some part of the carbide without connection with the original iron phase should decompose, the new iron phase formed there would have a very low content of the graphitizing substance.

The dilution theory is referred to only in order to point out that there is still no conclusive proof of the metastability of iron carbide in pure iron-carbon alloys at high temperatures. Thus it is pertinent indeed to reinvestigate the problem as one of the authors, Dr. Wells, has done in a recent paper, which forms the basis of an important part of the present paper. In constructing the curve of the carbon content in austenite saturated with graphite at temperatures above  $900^\circ\text{C}$ ., Dr. Wells has used two experimental results obtained by Gutowsky in 1907. His reason for choosing these old values is not convincing. It is not necessary that this curve and the corresponding carbide curve should be quite straight lines. Some little change in curvature may change their intersection temperature rather much.

An attempt has been made several times to use gas equilibrium experiments for determining whether the carbide is metastable or stable. In the present paper an equation used by Kelley is discussed, which is based upon an experimental investigation by Watasé of the equilibrium  $3\text{Fe}(\alpha) + \text{CH}_4 = \text{Fe}_3\text{C} + 2\text{H}_2$ . The experiments were limited to a temperature range between  $450^\circ$  and  $603^\circ\text{C}$ . Considerable courage is necessary for extrapolating from these rather low temperatures to temperatures as high as  $1200^\circ\text{C}$ . Nevertheless, Kelley calculated  $\Delta H - T\Delta S^*$  for the reaction  $3\text{Fe}(\text{pure } \gamma) + \text{C}(\text{graphite}) \rightarrow \text{Fe}_3\text{C}(\text{pure})$ . He found  $\Delta H - T\Delta S = 0$  for  $T =$

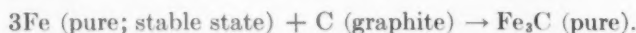
<sup>22</sup> *Jernkontorets Annaler* (1930) 431.

\* In the United States the function  $H - TS$  is usually denoted by  $F$ ; in Europe it has been recommended that this function shall have the symbol  $G$ , in honor

273 + 1207 and concluded that the carbide was stable at all temperatures above 1207°C. In the present paper the authors have rightly pointed out that the dilution of the gamma iron with carbon causes the carbide to be stable at temperatures above that at which  $\Delta H - T\Delta S = 0$ . It might be added that the correct conclusion from Kelley's equation, if it be accepted as reliable, is that iron carbide is not stable at any temperature.

Evidently there is good reason for an attempt to calculate  $\Delta H - T\Delta S$  in some different way, for instance on the basis of measurements of the heat of reaction at room temperature and of the heat capacities at low temperatures, as the authors have done in the present paper. But I believe that the limits of the accuracy possible in such a calculation will stand out more clearly if an arithmetically different method is applied.

The reaction may be written



It is not necessary to specify the phase state of the graphite, as recent investigations<sup>23</sup> indicate that the difference between alpha and beta graphite is fictitious. The transformation in iron carbide in the range from 150° to 250°C. is no phase transition and the properties of the carbide are continuous functions of the temperature.

The stipulation that the iron shall be in the state that is stable at the temperature of the isothermal isobaric reaction is chosen in order to avoid the calculation with unrealizable states. The heat of reaction  $\Delta H$  may then be treated as a single function of temperature, and this is very convenient for the graphical representation.

If the activities are referred to the states pointed out in the reaction formula as standards we have

$$-R \ln \frac{\{\text{Fe}_3\text{C}\}}{\{\text{Fe}\}^3\{\text{C}\}} = \frac{\Delta H}{T} - \Delta S$$

The pure iron carbide will be stable if its carbon activity is lower than unity, the graphite being assumed not to dissolve iron in measurable amounts. The carbide activity  $\{\text{Fe}_3\text{C}\}$  is equal to unity. The iron activity  $\{\text{Fe}\}$  of an iron phase saturated with iron carbide is lower than unity on account of carbon dissolved. The condition of carbide stability may thus be written

$$3R \ln \{\text{Fe}\} > \frac{\Delta H}{T} - \Delta S$$

If the values of the heat of reaction and the entropy change at 298°K.,  $\Delta H(298)$  and  $\Delta S(298)$ , are assumed to be known, the right side of the preceding equation may appropriately be found from the equation

$$\frac{\Delta H(T)}{T} - \Delta S(T) = \frac{\Delta H(298)}{T} - \Delta S(298) - \int_{298}^T \frac{\Delta H(T) - \Delta H(298)}{T^2} dT$$

The function  $\Delta H(T) - \Delta H(298)$  may be calculated from the  $C_p$  equations and the heats of transition as given by Kelley; the result is given by the dashed curve in Fig. 5. But it is generally difficult to find a reasonably simple equation that approximates the heat content of a real substance with sufficient accuracy, especially if transformations without phase change must be considered. A better approximation is probably obtained by using directly the experimental heat-content curves of the reacting sub-

of Gibbs (Report of a Joint Committee of the Chemical Society, the Faraday Society, and the Physical Society, 1937).

<sup>23</sup> Nat. Bur. Stds. *Jnl. of Research* (1938) **21**, 491.

stances; in this way the solid curve of Fig. 5 has been deduced.\* The integration is preferably made graphically by plotting  $(\Delta H(T) - \Delta H(298))/T^2$ . By this method the curves of Fig. 6 have been obtained from the corresponding curves of Fig. 5.

The entropy change  $\Delta S(298)$  may be deduced from the heat capacities at low temperatures. When discussing previous work on the heat capacity of iron carbide

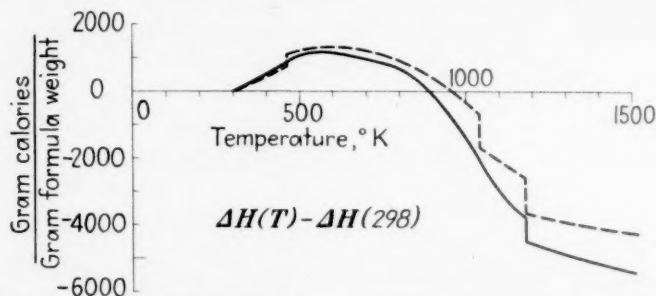


FIG. 5.—CURVES CALCULATED FROM KELLEY'S DATA (DASHED LINE) AND FROM EXPERIMENTAL HEAT-CONTENT CURVES OF REACTING SUBSTANCES (SOLID LINE).

the authors have undervalued the experimental results of Naeser. It is true that his heat-capacity values are obviously incorrect but, as Schwarz and Ulich have shown, this is caused by the use of an inappropriate arithmetical method. Schwarz and Ulich recalculated the heat capacity and obtained values that differ very little from those obtained by Andes. Their value of the entropy of  $\text{Fe}_3\text{C}$  is  $S(298) = 23.9$ , whereas Andes reported 23.55 and the present authors 25.7.

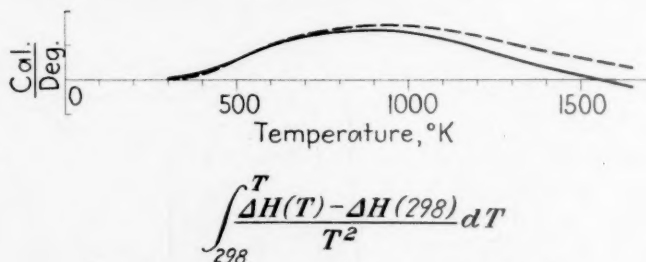


FIG. 6.—PLOTTED FROM CURVES OF FIG. 5.

The sample used by the authors for the determination of the heat capacity contained only 21 per cent carbide. Thus it was necessary to subtract heat capacity of 79 per cent alpha iron from the direct experimental result. For this purpose the results of Simon and Swain have been evaluated. It is a matter of fact that the results on heat capacity from two laboratories often differ much more than should be expected when the good consistency within each series of results is considered. Hence, when such a quantity is to be obtained as a difference between two rather great numbers, these numbers ought to have been determined with the same apparatus. If, in spite of these objections, the three values are given the same weight, the mean value is 24.4. Then we may assume

$$\Delta S(298) = 24.4 - 3 \times 6.49 - 1.37 = 3.6.$$

\* The heat content curve used for the carbide is due to Naeser and the corresponding curve for the iron was calculated from observations by Klinkhardt. The probability of a great relative error in the difference between the heat contents of  $\text{Fe}_3\text{C}$  and  $3\text{Fe} + \text{C}$  would have been smaller if these quantities had been determined by the same investigator.

The heat of reaction at ordinary temperature  $\Delta H(298)$  is even less accurately known. The calorimetric determination is very difficult, and the results published differ greatly. The authors have cited Roth for the value  $\Delta H(298) = 5400$  gram cal. The history of this value is rather interesting. Roth found in his own calorimetric work  $\Delta H(298) = 3900$ . He then accepted 5400 as the mean value of 3900 and 7000. The latter value was assumed to have been given by Watasé in 1928. In fact, Watasé did not report 7000 but 4800 in that paper. In 1930 Watasé recalculated  $\Delta H(298)$  from his previous experimental results, now using Roth's own values for the heat of formation of the iron oxides, and he obtained the result 2500. The mean value of 3900 and 2500 is 3200.

The authors have also mentioned a value of 5600 reported by Naeser. This was obtained by a wet solution method. It is well known that such methods are extremely difficult. In this case the carbon was left as an amorphous solution rest, the heat content of which was determined by comparison of its heat of combustion with that of graphite. This determination must be rather unreliable, hence very little weight ought to be ascribed to the value 5600.

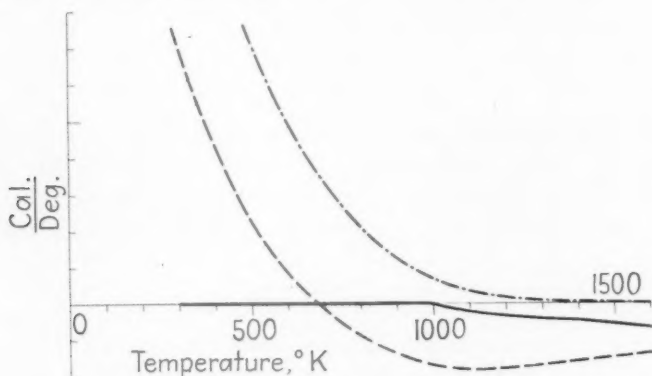


FIG. 7.

In Fig. 7 the dashed curve represents  $\Delta H/T - \Delta S$  as a function of temperature on the assumptions that  $\Delta H(298) = 3200$ ,  $\Delta S(298) = 3.6$  and also that  $\Delta H(T) - \Delta H(298)$  varies with temperature as shown by the full curve in Fig. 5. The carbide stability condition deduced before is

$$3R \ln \{Fe\} > \frac{\Delta H}{T} - \Delta S$$

The left side is negative, because  $\{Fe\} < 1$ . Up to the eutectoid temperature 998°K. it differs very little from zero because of the very small carbon content of alpha iron. For gamma iron at 998°K. the activity  $\{Fe\}$  is the same as for the alpha iron. When the temperature is further increased  $\{Fe\}$  decreases, the gamma iron saturated with carbide being now not in equilibrium with alpha iron. From 1183° to 1403°K. the iron is in the gamma state and the activity is referred to pure gamma iron. From observations by Dünwald and Wagner<sup>24</sup> it is evident that  $\{C\}$  is approximately proportional to the carbon content. It follows that  $\{Fe\}$  is approximately equal to the mol fraction of Fe in the gamma iron. Thus at 1183°K. we obtain  $3R \ln \{Fe\} = 13.7 \log 0.948 = -0.32$ , and at 1403°K.  $3R \ln \{Fe\} = 13.7 \log 0.926 = -0.46$ . At temperatures from 1403° to 1673°K. the iron phase is liquid but  $\{Fe\}$  is still referred to pure gamma iron. The liquid phase is not even approximately a dilute solution and it can only be stated that the temperature derivative of  $\{Fe\}$  has a somewhat greater negative value above than below 1403°.

<sup>24</sup> Dünwald and Wagner: *Ztsch. anorg. Chem.* (1931) **199**, 321.



In Fig. 7 the values of  $3R \ln \{Fe\}$  at different temperatures are represented by the full curve. Obviously the dashed curve representing  $\Delta H/T - \Delta S$  as calculated from the calorimetric results implies that the carbide should be stable at all temperatures above  $680^\circ K$ . But this is contradictory to the experimental fact that the pure carbide may decompose at temperatures above  $1000^\circ K$ . The only possibility is that the values assumed for  $\Delta H(298)$  or  $\Delta S(298)$ , or both, are incorrect. We may try the values assumed in the present paper,  $\Delta H(298) = 5800$  and  $\Delta S(298) = 3.73$ , in connection with the assumption that  $\Delta H(T) - \Delta H(298)$  is represented by the full curve in Fig. 5; then the dash point curve of Fig. 7 is obtained. This curve obviously is a better approximation to the real conditions than the first one, as it does not intersect with the curve  $3R \ln \{Fe\}$  below  $1000^\circ K$ . In fact, the curves do not intersect at all; that is, the carbide should be metastable at all temperatures. This difference from the result in the present paper is caused by the different assumption about the temperature function  $\Delta H(T) - \Delta H(298)$ , as shown in the Figs. 5 and 6.

It is evident that the accuracy of the present calorimetric result is not sufficient for any conclusions about the stability or metastability of iron carbide. The accuracy necessary in  $\Delta H(298)$  should be something like  $\pm 150$  gram cal. per gram formula weight, and this accuracy will be extremely difficult to attain. The entropy change  $\Delta S(298)$  ought to be determined with an accuracy of  $\pm 0.1$  cal. per degree centigrade; it will further be necessary to redetermine  $\Delta H(T) - \Delta H(298)$ .

H. SELTZ, H. J. McDONALD AND C. WELLS (authors' reply).—Professor Phragmén stresses the fact that  $Fe_3C$  is metastable at all temperatures below the eutectic in gray cast iron. This is, of course, precisely the conclusion reached by Wells (ref. 18) in his graphitization studies. We have emphatically stated that, *relative to gamma iron saturated with carbon and pure graphite*,  $Fe_3C$  is metastable up to the extrapolated intersection of the graphite and  $Fe_3C$  solubility curves at somewhere in the neighborhood of  $1200^\circ C$ . This, however, should not be confused with the stability of  $Fe_3C$  relative to *pure* gamma iron and pure graphite. From the solubility curves by sound thermodynamic methods, we have shown that for this reaction  $Fe_3C$  is stable above  $809^\circ C$ . The solubility data of Gutowsky were not used in our calculations. Wells merely pointed out that these data were in good agreement with the values found in his investigation. If Professor Phragmén accepts the solubility values used in our calculations, the conclusions we have reached concerning  $Fe_3C$  in this region must also be accepted. Any discussion of the influence of silicon on the decomposition of the carbide is of interest but is not pertinent to this work. It should be noted further that neither the entropy value determined by the authors from low-temperature measurements nor the reported  $\Delta H$  values at  $298^\circ K$ . were used in this paper to calculate the thermodynamic properties of iron carbide. We show merely that our entropy value is in satisfactory agreement with that obtained from the calculations at high temperatures. Professor Phragmén's use of the activity function seems a bit obscure. If  $Fe_3C$  is a definite "ordered" compound, it does not seem desirable to speak of the activity of carbon and iron in it any more than one would speak of the activity of carbon in carbon dioxide or of sodium in sodium chloride. The activity is defined by the relation  $RT \ln a = \bar{F} - F^\circ$ , where  $\bar{F}$  is the partial molal free energy of the component in a phase and  $F^\circ$  is the molal free energy at some reference state. In pure  $Fe_3O$  the value of  $\bar{F}$  for carbon is  $-\infty$  and hence the activity is zero. To state that " $Fe_3C$  is metastable if its carbon activity exceeds that of graphite" has no thermodynamic significance. The *over-all* free-energy change of the decomposition reaction alone determines the direction of reaction. As we have shown,  $Fe_3C$  above  $809^\circ C$ . cannot decompose into pure gamma iron and pure carbon, since the free energy change for this reaction here is positive. On the other hand, at the same temperature it can and does decompose into austenite, saturated with carbon, and free carbon, since the partial molal free energy of iron in austenite is less than that of pure gamma iron.



## Rate of Diffusion of Carbon in Austenite in Plain Carbon, in Nickel and in Manganese Steels

BY CYRIL WELLS\* AND ROBERT F. MEHL,† MEMBERS A.I.M.E.

(New York Meeting, February 1940)

THE diffusion of carbon in gamma iron plays an essential role in many metallurgical processes. In carburizing, in graphitizing, in homogenizing, in the formation of pearlite from austenite, and in other processes, migration of carbon in gamma iron occurs.<sup>1,2</sup> A full understanding of the rate at which these processes occur obviously requires a knowledge of the rate of diffusion of carbon. In carburizing, for example, the depth of carbon penetration is determined by the carbon concentration in solid solution at the surface, and by the rate of diffusion inward of the carbon. Until reliable data on the rates of diffusion of carbon are available it is unlikely that a full quantitative description of this process will be obtained. In the formation of pearlite from austenite, the segregation of carbon and alpha iron from the austenite obviously requires the diffusion of carbon; the rate at which pearlite nodules grow is evidently controlled at least in part by the rate of diffusion of carbon; it is unlikely that we shall understand the factors that determine the rate of growth unless data on rates of diffusion of carbon, and the variation of these with composition, grain size, and temperature are available. Accordingly it was decided: (1) to determine, more accurately than hitherto, the diffusion coefficients of carbon in austenite over a wide temperature and a wide concentration range, (2) to study the influence of grain size and impurities on this diffusion coefficient, and (3) to study the effect of manganese and nickel on the rate of diffusion of carbon in the austenite of manganese and nickel steels, respectively; the influence of carbon on the rate of diffusion of manganese and of nickel will be made the subject of later papers.

The rate of diffusion of carbon in gamma iron has been studied by Runge<sup>3</sup> by Tammann and Schönert<sup>4</sup>, by Bramley and co-authors,<sup>5-14</sup> and

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Manuscript received at the office of the Institute Dec. 1, 1939. Issued as T.P. 1180 in METALS TECHNOLOGY, August 1940.

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<sup>1</sup> References are at the end of the paper.

by Paschke and Hauttmann.<sup>15</sup> Runge determined  $D$ ,\* the diffusivity coefficient, at 930°C., Tammann and Schönert at 925°C. and 1000°C., Bramley covered a temperature range of about 200°C. (from the  $A_3$  temperature in Fe to 1100°C.), and Paschke and Hauttmann a range of about 350°C. ( $A_3$  to 1250°C.). Runge gas-carburized wire specimens, determining the change of electrical resistance with time during the carburization period. He assumed that early in this period the wire surface became saturated with carbon and that thereafter the concentration at this point remained constant. If this assumption is not correct (and Bramley's work seems to show it is not), Runge's  $D$  values are doubtful. Tammann and Schönert, who also gas-carburized specimens, made the same assumption, and their results are similarly doubtful. Furthermore, Tammann and Schönert used a microscopic method to determine the perpendicular distance from a polished carburized surface to the mid-point of the pearlitic region, assumed to contain 0.9 per cent C. Their calculated  $D$  values were much higher than those of other investigators, owing partly no doubt to this mode of evaluating concentration, since it is now known that the eutectoid composition in plain carbon steels is closer to 0.8 per cent than to 0.9 per cent C, and since it is now known that pearlite may be formed alone over a fairly wide range in carbon concentration when the rate of cooling is rapid, thus rendering an appraisal of a particular concentration uncertain.

Bramley and co-authors carburized iron and decarburized steel specimens and determined the carbon concentrations at various depths from the surface. In these determinations of  $D$  a solution, or a combination of solutions of Fick's law was used. If the meaning of the terms in the equations used, and the conditions to be met experimentally before these should be applied are considered, it may be observed that these conditions were in fact not met experimentally.† The values of  $D$  determined by Bramley are questionable.

Of the methods used in the study of the rate of diffusion of carbon in

\* The diffusion coefficient is usually designated by  $D$ . This represents the amount of substance in grams diffusing in one second across an area of 1 sq. cm. through a unit concentration gradient (ref. 1, p. 3).  $D$  has dimensions of length squared divided by time.

† For example, one solution much used was  $\phi = \frac{H}{2\sqrt{\pi Kt}} \cdot e^{-\frac{x^2}{4Kt}}$  where  $\phi$  = concentration of carbon above that initially present in the steel, at a depth  $x$  below the surface,  $t$  = time of diffusion,  $K$  = diffusion constant and  $H$  a numerical constant. This equation shows the carbon distribution that would result if all the carbon (amount  $H$ ) to be diffused were released at the surface in a sudden surge at the beginning of carburization, and none thereafter. Obviously this condition did not exist in any of Bramley's experiments. Bramley apparently selected this solution because it gave a form of diffusion-penetration curve simulating that observed. It is doubtful whether any solution could be selected to represent the constantly changing surface concentrations that occurred in Bramley's experiments.

gamma iron, that used by Paschke and Hauttmann is beyond question the best. A cylindrical piece of a high-carbon steel (1.1 per cent C) was welded end to end to a similar piece of Armco iron and the carbon distribution across the weld after a diffusion-anneal was determined. The Grube<sup>16</sup> and the Stefan<sup>17</sup> methods were used to calculate the  $D$  values. The main advantages of this method are: (1) the effect of impurities and of alloying elements on the rate of diffusion of carbon in steels can be quantitatively controlled at will, (2) radial diffusion is avoided, (3) the requirements for the application of standard solutions to Fick's law may be readily met, and (4) the question of the rate of absorption of carbon at a gas-specimen interface is avoided.

All previous workers have tacitly assumed that  $D$  does not vary with carbon concentration, and accordingly have given  $D$  values without reference to the compositions to which they pertain. Since, however, it is known that  $D$  may vary widely with concentration in other systems,<sup>1</sup> and since it will be shown that  $D$  does in fact vary with concentration in the gamma Fe-C solid solution, the previously reported values if correct at one carbon concentration must be to a certain degree in error at all others. The application of the Grube solution will not lead to serious error if  $D$  does not vary greatly with concentration, but the application of the Stefan method<sup>1</sup> is inadvisable, for the boundary conditions for this solution may be seen to be clearly violated from the types of diffusion-penetration curves obtained. Paschke and Hauttmann report the results obtained to be in agreement irrespective of the solution used. Apparently the data were not sufficiently precise to detect the error that would inevitably result from the use of the Stefan solution.

Paschke and Hauttmann did not attempt to discover whether or not the austenite grain size affects the diffusivity coefficient. The effect of impurities usually present in commercial steel was studied by Bramley, who reported that 0.2 per cent sulphur lowers the rate of diffusion appreciably; phosphorus and oxygen were reported to have a slight effect, and nitrogen practically no effect. Tammann and Schönert reported that impurities affect the rate of diffusion of carbon very markedly, but their results may be open to question, because of the low sensitivity of the method used to determine  $D$  values. They also found that manganese and nickel from 0 to 10 per cent slightly increase and from 10 to 20 per cent slightly decrease the depth of carbon penetration upon carburization.

#### EXPERIMENTAL

*Composition of Materials.*—The compositions of the iron, the plain-carbon steels, and the alloy steels used in the present investigation are listed in Table I. These differ considerably in purity, including high-purity steels especially prepared, ordinary commercial steels containing the usual impurities of such steels, and other specially prepared alloys,

TABLE 1.—*Composition of Alloys<sup>a</sup>*

Alloy No.	Composition, Per Cent								Remarks
	C	P	S	Si	Mn	Cu	Ni	O <sub>2</sub>	
A1	0.02	0.005	0.028	0.004	0.030	0.132			Armco iron.
A2	0.02	0.005	0.030	0.008	0.030	0.090			Armco iron.
B3	1.07	0.017	0.036	0.070	0.40				Aluminum-killed steel.
A4 <sup>b</sup>	0.01	<0.005	<0.001	<0.005	<0.005	0.006	0.040		Hydrogen-treated carbonyl iron.
A5	0.10	0.015	0.030	0.029	0.37				Aluminum-killed steel.
B6	0.13	0.012	0.023	0.020	0.49				Completely graphitized steel.
B7	0.59	0.009	0.009	0.030	0.003	0.003	0.002		Melted under hydrogen.
A8	0.25	<0.005	<0.005	<0.005	2.50	0.006	0.005		High-purity manganese steels. Melted under argon.
B9	1.19	<0.005	<0.005	<0.005	2.54	0.012	0.002		
A10	0.04	<0.005	<0.005	<0.005	16.0	0.012	0.003		
B11	1.28	<0.005	<0.005	<0.005	15.8	0.032	0.009		
B12	0.47	0.020	0.028	0.26	1.81				Aluminum-killed steel.
A13	0.23	0.015	0.025	0.25	1.97				
A14	0.28	0.014	0.036	0.053	0.45				
B15	0.80	0.039	0.024	0.27	0.46				
A16	0.43	0.017	0.030	0.21	0.85				Nickel and Armco iron melted together.
A17	0.63	0.016	0.033	0.16	0.67				
A18	0.27	0.014	0.025	0.21	0.45	0.082	1.9		
B19	1.36	0.019	0.022	0.37	0.66	0.080	1.9		
B20	0.60	0.027	0.025	0.27	0.56	0.078	1.9		Nickel and Armco iron melted together.
B21	0.60	0.025	0.017	0.26	0.52	0.060	20.0		
A22	0.06	0.009	0.020	0.12	0.28	0.100	20.3		Vacuum melted Armco iron to which oxygen had been added.
A23	0.006	0.006	0.020	0.005	0.008	0.040	<0.005	0.19	
A24	0.03	0.003	0.003	0.003	0.010	0.036	0.010	0.003	Vacuum melted electrolytic iron.

<sup>a</sup> Alloys 23 and 24 contained 0.004 and 0.002 per cent N<sub>2</sub>, respectively.

<sup>b</sup> This iron was purified by heating in hydrogen for 750 hr. at 1200°C. Cr, Sn and Mo were present as spectroscopic traces. In similar iron these elements taken together gave a total of less than 0.005 per cent. Hydrogen also was present to the extent of 0.0005 per cent.



some high in purity, some deliberately low. The iron-nickel-carbon alloys are rather impure, containing about 0.2 per cent silicon and 0.5 per cent manganese; the iron-manganese-carbon alloys are much purer than commercial manganese steels.

*Experimental Procedure.*—The method used to determine concentration-penetration curves, to be used in the calculation of  $D$  values, consists essentially of: (1) the preparation of specimens by welding steels of differ-

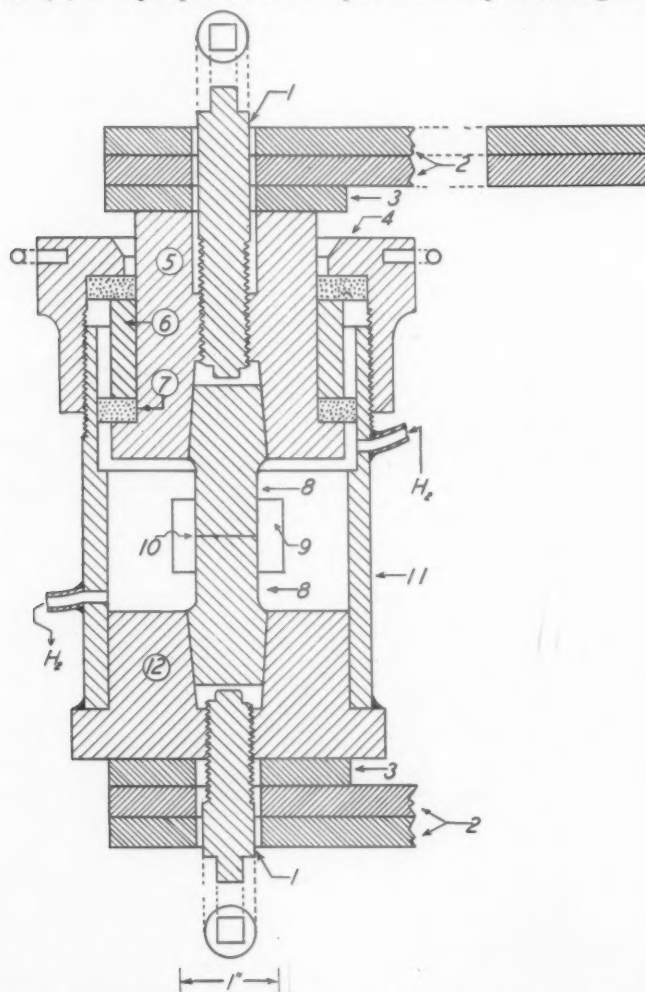


FIG. 1.—WELDING APPARATUS (DRAWN ROUGHLY TO SCALE).

1. Screws for pushing specimen from holder.
2. Heavy copper leads to transformer.
3. Copper ring.
4. Steel top, threaded inside. Allows 1, 2, 3, 4, 5, 6 and 7 to be lifted as a unit when the welded specimen is to be removed.
- 5 and 12. Steel parts that hold specimen in place and prevent overheating.
6. Steel ring.
7. Transite board insulator.
8. Specimen.
9. Mica window in 11.
10. Position of weld.
11. Outer steel case (welded to part 12).
12. End piece.

ent carbon contents, (2) the annealing of these in order to diffuse carbon along the specimens across the welded "interface," and (3) the determination of the carbon distribution across the diffusion zone and the



plotting of concentration-penetration curves. This is the experimental method employed by Paschke and Hauttmann.

*Preparation of Specimens.*—These were made by welding, as stated. The specimens were cylindrical, of 1-in. dia. in some cases and  $\frac{5}{8}$ -in. in others, and tapered at the ends. The surfaces to be welded were machined flat and perpendicular to the cylindrical axis. They were then rubbed on fine emery cloth and finished on 000 metallographic paper to render them smooth; they were finally washed in alcohol and carefully dried to prevent staining. The two prepared parts of the specimen were put into the welding apparatus (Fig. 1). The prepared surfaces were held very closely parallel and were pressed tightly together by screwing

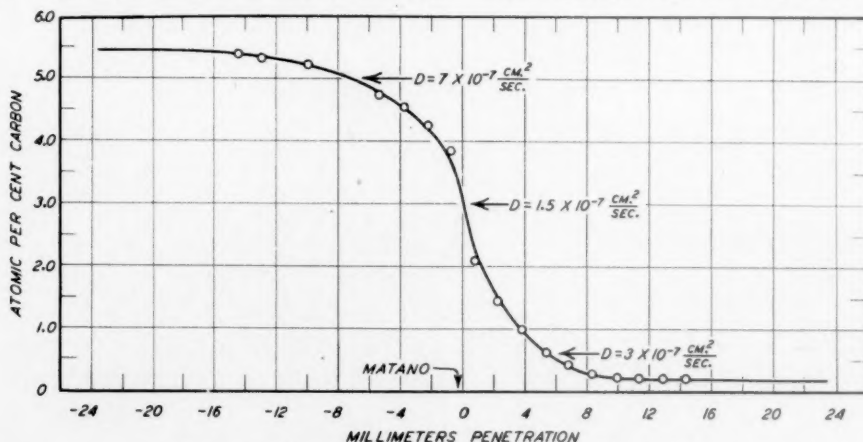


FIG. 2.—CONCENTRATION-PENETRATION CURVE.

This curve and that of Fig. 3 show by irregularity in the neighborhood of the interface the effects of a poor weld. Alloy B11 was welded to A10 and subsequently heated at 1005°C. for 72 hours.

down the top of the apparatus. A stream of hydrogen or helium was passed around the specimen to prevent oxidation during welding. The voltage across a specimen was of the order of 4 to 6 volts\* and the amperage 5000 amp. The time of application of the current varied between 20 sec. and 1 min., depending on the size and composition of the pieces being welded. When the current was shut off the specimens cooled to below 500°C. in less than 1 minute.

Of about 100 specimens prepared, only two were poorly welded. A weld was considered good: (1) if no evidence of holes could be discovered in the weld on careful microscopic examination, (2) if machined turnings taken from this region were mechanically continuous (which was found to be a good test for continuity across the weld), and (3) if, after subsequent annealing, the carbon distribution across the diffusion zone showed no special inflection or change in slope. A comparison of the curves given in Figs. 2 and 3 shows the effect of a poor weld on the con-

\* Power was delivered from a suitable transformer. The voltage across the primary could be varied between 0 and 440 volts.

centration-penetration curve. Good results were obtained as well with high-alloy steels as with plain carbon steels (Figs. 4 and 5). Fig. 4 also gives some indication of the extent of carbon diffusion from the high-carbon to the low-carbon alloy during the welding operation. In another

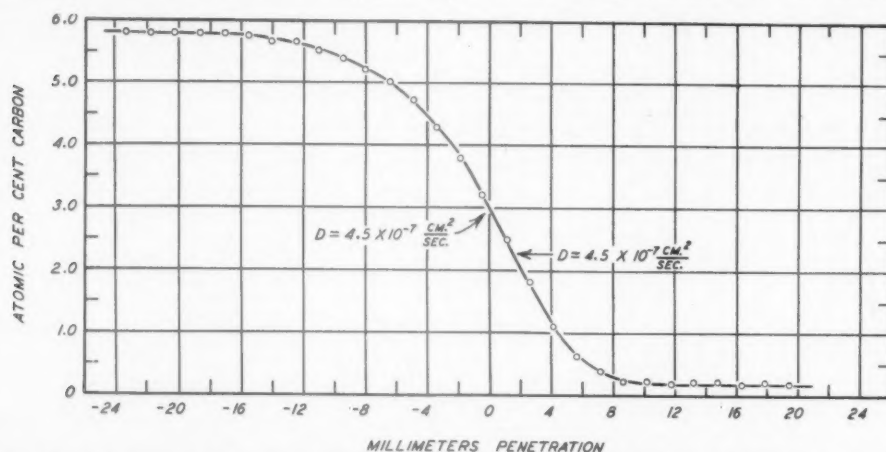


FIG. 3.—CONCENTRATION-PENETRATION CURVE SHOWING VARIATION IN CARBON CONCENTRATION IN A HIGH-MANGANESE STEEL (16 PER CENT Mn).

Alloys B11 and A10 were welded (good weld) and subsequently heated at 1005°C. for 72 hours. (Test 34.)

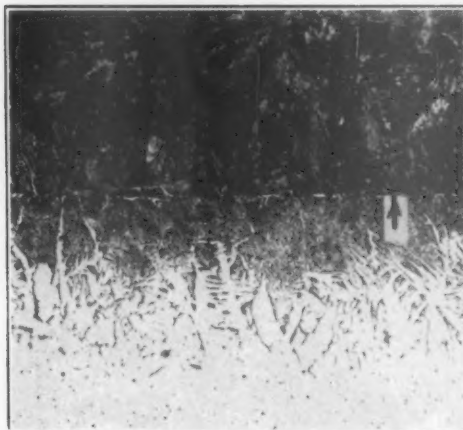


FIG. 4.

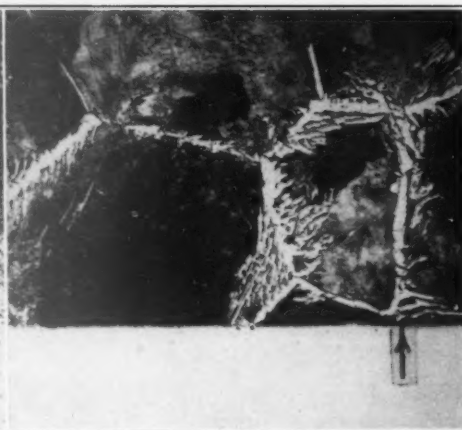


FIG. 5.

FIG. 4.—ALLOY A3, 1.07 PER CENT CARBON, WELDED TO ARMCO IRON, A23 (0.006 PER CENT CARBON, 0.19 PER CENT OXYGEN). WELDING TIME ONE MINUTE.  $\times 100$ .

Etched with nital. Arrow indicates position of weld. Shows evidence of good weld. Extent of carbon penetration into Armco iron as observed microscopically about 0.2 mm.

FIG. 5.—NICKEL STEELS WITH 0.25 PER CENT CARBON EACH AND NICKEL 20.0 AND 1.9 PER CENT, RESPECTIVELY, WELDED. WELDING TIME 20 SECONDS.  $\times 300$ .

Etched with nital. Arrow indicates position of weld. Shows evidence of good weld. High-nickel alloy at bottom was unetched.

test it was found that the carbon concentration in a low-carbon alloy increased from 0.13 to 0.41 atomic per cent carbon at a distance of about 0.2 mm. from the weld. This amount of penetration is negligible; calculation shows that this is about equivalent to that which would result

from a heat-treatment of 15 min. at 800°C. or of 1 min. at 1050°C., time periods that in every case are negligible to the time periods of the diffusion-anneal.

*Diffusion-anneal.*—Specimens were heated in argon or in vacuum\* (one in hydrogen) at the temperatures and for the times recorded in Table 2 and subsequently were cooled in helium to below 600°C. in 5 min. The temperatures were controlled within 1°C. Time-temperature curves giving evidence of this close control have already been published.<sup>18</sup> The approximate number of austenite grains per square millimeter present

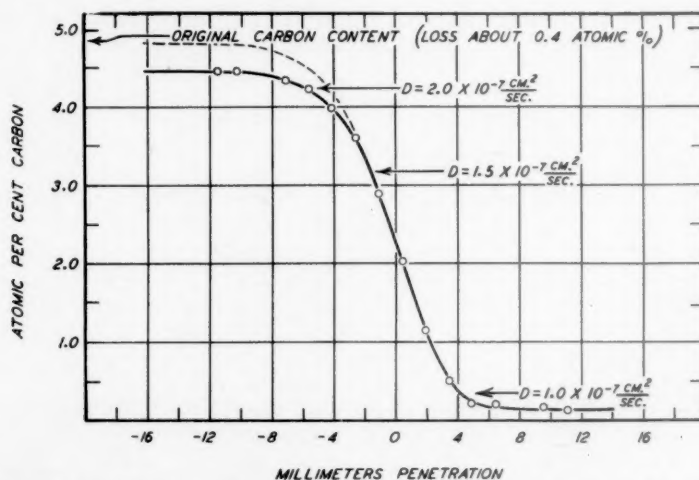


FIG. 6.—CONCENTRATION-PENETRATION CURVE SHOWING EFFECT OF SURFACE DECARBURIZATION.

Dotted curve shows concentration-penetration curve when no carbon is lost; full curve when loss is 0.4 atomic per cent. The calculated  $D$  values (range 0.4 to 4.2 atomic per cent) were little changed by the surface decarburization. (Compare Fig. 6 with Fig. 7, diffusion at 925°C.)

in the specimens at the end of the various heat-treatments are also recorded in Table 2.

Microscopic study showed that the specimens heated in argon or in a good vacuum were not appreciably decarburized. In one or two tests, however, too much oxygen was present in the system prior to admitting argon and some decarburization occurred (Fig. 6). From a comparison of the results given in Figs. 6 and 7, apparently a considerable loss of carbon can occur during annealing without appreciably changing the  $D$  values determined. It is surprising that this should be true over so large a range of carbon concentration.

As stated above the specimens were quickly cooled after the diffusion-anneal, though not quenched. Quick cooling was practiced because evidence was obtained showing that a redistribution of carbon occurred during slow cooling. Quenching was found unwise, for specimens

\* The total pressure was about 1 micron, but the partial pressure of air, and therefore of oxygen, was usually below 0.1 micron.

TABLE 2.—*Heat-treatment and Grain-size Data*

Test No.	Alloy A welded to Alloy B <sup>a</sup>		Temperature of Diffusion, Deg. C.	Time of Diffusion, Hr.	Approximate Average Number of Austenite Grains per Sq. Mm.	
	No. of Alloy A	No. of Alloy B			Alloy A	Alloy B
2	A10	B11	1005	72	<1	130 and 2 <sup>b</sup>
3	A4	B3	922	90	1(16)	100(2000) <sup>c</sup>
5	A4	B3	1005	21	<1(4)	30(1000)
6	A4	B3	1000	18.2	1(8)	30(1000)
7	A4	B7	1004	23.5	1(8)	10 and 30
8	A5	B3	1000	24	30	30
9	A2	B3	997	25.25	1	30(1000)
10	A2	B3	1001	42.66	1	30(1000)
11	A16	B15	798	227	2500	1000
12	A16	B15	800	200	2000	1000
13	A16	B15	800 <sup>d</sup>	213	40	20
14	A16	B15	801 <sup>d</sup>	330	40	20
15	A4	B6	925	40.5	1	
16	A4	B6 <sup>e</sup>	925	40.5	1	
17	A1	B3	924	20	<1	100(2000)
18	A2	B3	927	40	15	100(2000)
19	A1	B3	925	61.5	<1	30(2000)
20	A17	B15	755	242	1000	2000
21	A14	B15	850	170	100	500
22	A2	B3	946	65	10	60(1000)
23	A2	B3	1052	24	1 and 4	16(?)
24	A4	B3	1102	24	2(16)	16(16)
25	A4	B3	1148	12	1(16)	8(16)
26	A4	B3	1197	6.38	<1	4(4)
27	A4	B3	1245	6.35	<1	4
28	A18	B19	1004	72	2	2
29	A18	B20	1005	72	2	4
30	A22	B21	1000	64.5	30	60
31	A22	B21	999	18.1	30	60
32	A8	B9	998	24.6	1 and 4	8
33	A13	B12	1001	34	1000	150
34	A10	B11	1005	72	<1	130 and 2
35	A23	B3	1000	24	9	60(1000)
36	A24	B3	1000	26.5	4	60

<sup>a</sup> Analyses of alloys given in Table 1.

<sup>b</sup> Small and large grains were developed both close to and away from the weld.

<sup>c</sup> Figures in parentheses (probably only very approximately correct) refer to the grain sizes close to the weld (see Fig. 13a).

<sup>d</sup> Specimens in tests 13 and 14 were heated at 1100°C. for ½ hr. to develop large grain sizes before cooling at 800°C. (Figures given, 213 and 330 hr., are the corrected time figures.)

<sup>e</sup> Steel B6 in test 15 contained no carbide and in 16 no graphite prior to heating to the diffusion temperature.



quenched in water or in oil often contained quenching cracks and therefore exhibited some distortion.

*Determination of Carbon Distribution.*—Following the diffusion-anneal the outer layers of the bar were removed by machining in order to eliminate any decarburized surface. To determine with the utmost accuracy the distribution of carbon longitudinally in the cylindrical specimen, the thickness of each consecutive layer perpendicular to the longitudinal axis removed as turnings by machining for analysis was measured to within 0.0002 in. and the plane of the machined surface was kept as parallel as possible to the plane of the weld.\*

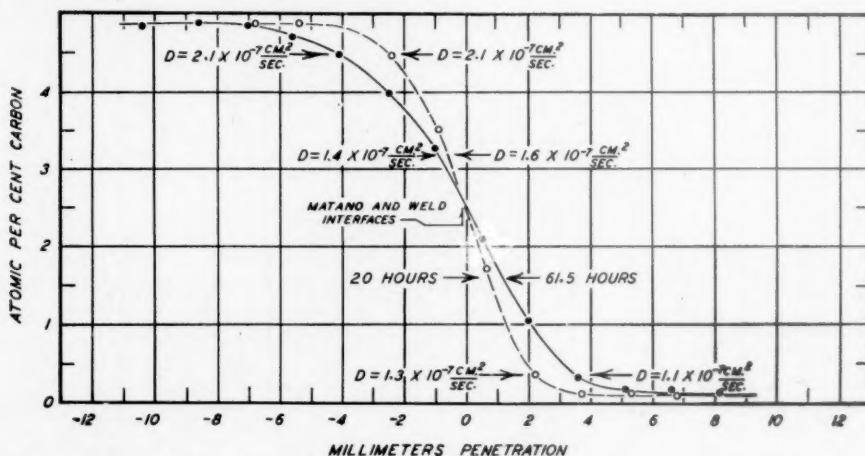


FIG. 7.—CONCENTRATION-PENETRATION CURVES SHOWING INFLUENCE OF TIME OF DIFFUSION-ANNEAL (925°C.) ON DISTRIBUTION OF CARBON. (TESTS 17 AND 19.)

The analyses should not be in error by more than 0.005 per cent, nor the distance measurements by more than 0.0002 in. (0.005 mm.). Typical data are plotted and typical concentration-penetration curves are drawn in Figs. 3 and 7.

## RESULTS

The  $D$  values calculated for various concentrations between 0.1 and 1.0 weight per cent carbon are given in Table 4.† The  $D$  values were calculated by the Matano and the Grube methods, previously described.<sup>1,19</sup>

\* Distances were measured between a hairline on the specimen and the flat machined surfaces left after each layer was removed. The hairline was in a plane parallel to the weld and on one side of it while the machined surfaces were on the other. All measurements agreed within  $\pm 0.0002$  inches.

† Table 3, which lists the original experimental data from which the diffusion-penetration curves were plotted and the diffusion coefficients calculated, has been issued through Auxiliary Publication and may be obtained from the American Documentation Institute, care Science Service, 2101 Constitution Ave., Washington, D. C., by ordering Document No. 1321, remitting 27¢ for copy in microfilm (read enlarged to full size on reading machines now widely available, or 90¢ for copy in paper photoprints legible without mechanical aid).



*Accuracy*

The  $D$  values determined in the present investigation are believed to be correct to within  $\pm 10$  per cent. Errors of temperature measurement and of chemical analysis are probably the most serious. Temperatures were measured to within  $\pm 3^\circ\text{C}.$ \* (the variation in temperature

TABLE 4.—*Diffusion Data, Carbon in Gamma Iron*

Test No.	Specimen Carbon Range Wt. Per Cent	Nickel Content, Wt. Per Cent	Manganese Content Wt. Per Cent	Temperature of Diffusion, Deg. C.	Diffusion Anneal in	$D \times 10^7 \text{ Cm.}^2 \text{ per Sec. at Various Concentrations (Wt. Per Cent)}$			
						0.10 <sup>a</sup>	0.54	0.70	1.00
5	0.01 -1.07			1005	Vacuum		(3.5) <sup>b</sup>	3.7	4.9
6	0.01 -1.07			1000	Hydrogen	3.0		3.3	
8	0.10 -1.07			1000	Argon		(3.2)	3.5	4.4
9	0.02 -1.07			997	Vacuum	2.6		3.2	3.9
10	0.02 -1.07			1001	Argon	2.6		3.3	4.8
11	0.43 -0.80			798	Argon		0.36	0.38 (0.35)	
12	0.43 -0.80			800	Vacuum		0.28	0.39	
13	0.43 -0.80			800	Vacuum		0.34	0.42 <sup>c</sup>	
14	0.43 -0.80			801	Vacuum		0.31	0.35	
19	0.02 -1.07			925	Argon	1.1	(1.4)	1.4 (1.6)	2.1 (2.0)
20	0.63 -0.80			755	Argon			0.18 (0.19)	
21	0.28 -0.80			850	Argon			0.66 (0.73)	
22	0.02 -1.07			946	Argon		(2.1)	2.0 (2.3)	
23	0.02 -1.07			1052	Argon	4.4	(5.5)	5.6 (5.7)	
24	0.01 -1.07			1102	Argon	7.7	(9.2)	10.0 (10.9)	14.0
25	0.01 -1.07			1148	Argon	10.1	(12.7)	13.5 (14.4)	17.3 (17.8)
26	0.01 -1.07			1197	Argon	12.9	(16.1)	19.0 (20.1)	25.0
27	0.01 -1.07			1245	Argon	19.4	(23.2)	25.7 (26.3)	31.2
28	0.27 -1.36	1.9		1004	Argon		4.1	4.3	5.6
29	0.27 -0.60	1.9		1005	Argon		3.8		
30	0.06 -0.60	20.0		1000	Argon	2.6	4.2		
31	0.06 -0.60	20.0		999	Vacuum	2.8	3.8		
32	0.25 -1.19		2.5	998	Vacuum		3.4	(3.7)	4.4
34	0.04 -1.28		16.0	1005	Argon	3.2	4.5	4.7	5.9
35	0.006-1.07			1000	Argon	2.5	(3.2)	3.5 (3.4)	3.9
36	0.03 -1.07			1000	Argon	2.1	(2.8)	3.1 (3.2)	4.6

<sup>a</sup> Atomic per cent carbon is about  $4.5 \times$  weight per cent over range studied.

<sup>b</sup> Matano method was used to calculate  $D$  values in parentheses and Grube method all other values.

<sup>c</sup> This figure may be too high, owing to loss of 0.04 weight per cent carbon during test.

was less than  $1^\circ\text{C}.$ ), and the accuracy of the carbon determinations was within 0.005 per cent.

Preliminary check tests using specimens of similar compositions gave  $D$  values, calculated at a number of concentrations, in agreement within 10 per cent. The results of two tests (Fig. 7) in which time was the only variable show: (1) about what reproducibility in calculated  $D$  values can be obtained, and (2) the reproducibility of the  $D$  values in relation to the carbon concentration for which they are calculated. In specimens con-

\* Wire, from which new thermocouples were made for each test, was calibrated frequently by standard methods, and several precautions<sup>22</sup> were taken to ensure the greatest possible accuracy.

taining between 0.03 and 1.07 weight per cent carbon at concentrations higher than about 1 per cent carbon (4.53 atomic per cent) and below 0.1 per cent carbon (0.45 atomic per cent), it was found that the calculated  $D$  values were in general relatively unreliable. The most reproducible values obtained are those calculated by the Matano method for a concentration range approximately 20 per cent of the total located midway between the maximum and minimum concentrations in the specimen. Outside this range, the Grube method probably gives as accurate results as the Matano. The relative unreliability of  $D$  values calculated from the ends of the concentration-penetration curve has been discussed in an earlier paper.<sup>19</sup>

Calculation shows that a 10 per cent error can be introduced into the  $D$  values by an uncertainty in the temperature of 5°. The effect of error in carbon analysis is more difficult to evaluate.<sup>19</sup> It depends on: (1) the total composition range in a specimen, (2) the concentrations at which  $D$  values are calculated, and (3) the concentration gradients existing there. In the present work, the total concentration range was in all cases, except in tests 15 and 16, large enough and the gradients of such values over the middle 20 per cent or so of the total range that the  $D$  values (Matano method) were not changed by more than about 3 per cent, owing to an error of 0.005 per cent in carbon analysis. At concentrations outside of the central 20 per cent range but within the 80 per cent range the  $D$  values calculated by either the Matano method or the Grube method do not change by more than 5 per cent owing to an error of 0.005 per cent carbon. At concentrations lying outside of 90 per cent of the total concentration range the  $D$  values calculated by either method are unreliable. Errors of measurement of time and distance were so small as to have practically no effect on the results obtained and thus can be disregarded. The errors caused by preliminary diffusion occurring during welding and by loss of carbon during annealing are negligible. No  $D$  value was accepted if it was based upon the results of any test in which more than 0.03 per cent C was lost from the high-carbon end of the specimen; generally the loss of carbon in tests was 0.01 per cent or less. A minor error may result from heterogeneity, particularly with respect to alloying elements, in the alloys used. In preliminary work some of the high-manganese steels were homogenized, but it soon became evident that the effect of both manganese and nickel on the rate of diffusion of carbon in gamma iron is so small that homogenization treatments seemed unnecessary. Microscopic studies showed a uniform distribution of carbon and the absence of appreciable dendritic segregation in the high-manganese and high-nickel steels. Chemical analyses of consecutive layers, only 0.003 in. thick, taken from the manganese and nickel steels showed the concentration of these elements not to vary appreciably from layer to layer.

## DATA

In high-purity steels we may inquire how  $D$  varies with concentration and temperature and with grain size; in commercial steels we shall in addition wish to know the effect upon  $D$  of the amount and distribution of impurities; in alloy steels we shall wish to know the effect upon  $D$  of the

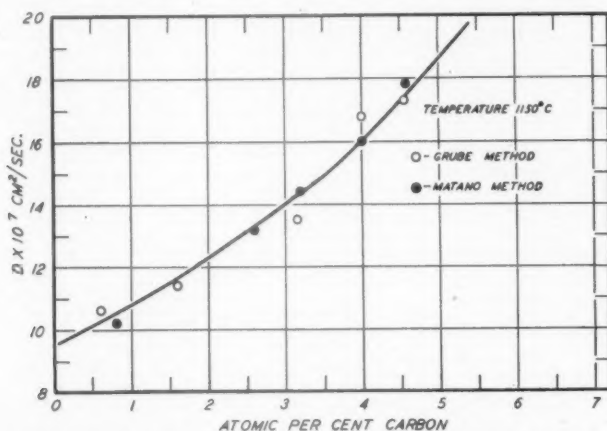


FIG. 8.—COMPARISON OF  $D$  VALUES AS CALCULATED BY GRUBE METHOD AND BY MATANO METHOD.

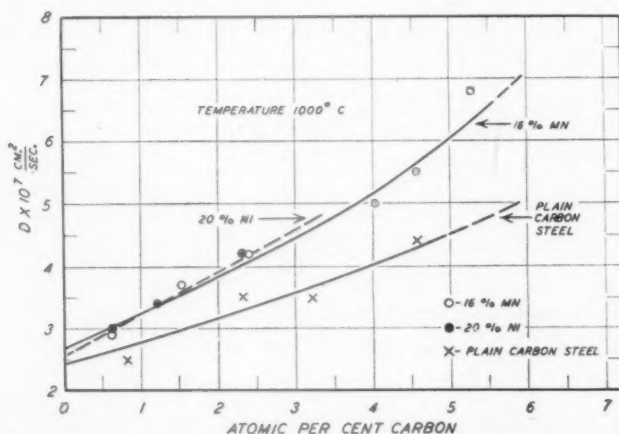


FIG. 9.—EFFECT OF CARBON CONCENTRATION ON  $D$  IN PLAIN CARBON STEELS, MANGANESE STEELS (16 PER CENT MANGANESE), AND NICKEL STEELS (20 PER CENT NICKEL).

Data taken from tests 8, 30 and 34, and  $D$  values at 1000°C. calculated.

alloying elements, and in particular that of nickel and of manganese. The results of the study of each of these variables is given below.

The calculated diffusion coefficients are listed in Table 4. Though  $D$  may be calculated for any carbon concentration upon the concentration-penetration curve, for purposes of ready comparison  $D$  values at 0.1 per cent C (0.45 at. per cent), at 0.54 per cent C (2.45 at. per cent), at 0.7 per cent C (3.18 at. per cent) and at 1.0 per cent C (4.53 at. per cent) are listed. It may be observed from these data that  $D$  increases regularly as

the carbon concentration is increased, the rate of increase being somewhat higher at the higher concentrations. At 925°C. (test 19) the increase is from  $1.1 \times 10^{-7}$  cm.<sup>2</sup> per sec. at a concentration of 0.1 wt. per cent C to  $D = 2.1 \times 10^{-7}$  cm.<sup>2</sup> per sec. at a concentration of 1.0 wt. per cent C. At 1102°C. the increase is from  $7.7 \times 10^{-7}$  cm.<sup>2</sup> per sec. to  $14.0 \times 10^{-7}$  cm.<sup>2</sup> per sec. (test 24), at 1197°C. from 12.9 to  $25.0 \times 10^{-7}$  cm.<sup>2</sup> per sec. (test 26), and at 1245°C. from 19.4 to  $31.2 \times 10^{-7}$  cm.<sup>2</sup> per sec. (test 27). It may be observed from these data that the percentage increase in  $D$  with carbon concentration is approximately a constant over a wide temperature range. The  $D$  values increase about 80 per cent as the concentration is changed from 0.1 to 1.0 weight per cent carbon. The increase of the diffusion coefficient with increase in carbon concentration is shown graphically in Figs. 8 and 9. A similar but slightly higher rate of increase of  $D$  with carbon concentration was observed in the manganese and nickel steels (Fig. 9).

*Effect of Grain Size.*—Grain sizes in the steels studied range from less than one (A.S.T.M. grain size No. -3) to more than 2000 grains per square millimeter (A.S.T.M. grain size No. 8), which includes practically all of the grain sizes encountered in plain carbon and alloy steels.

When the logarithms of the  $D$  values are plotted against  $1/T$ , where  $T$  is the absolute temperature of diffusion anneal, the points all fall on a straight line within experimental error. This indicates that while  $D$  changes with  $T$  (temperature) in the generally accepted manner, a change of grain size from 2000 (tests 11, 12, and 20, Table 2) to one grain per square millimeter (test 27) had no appreciable effect.

In order to study the influence of grain size upon the rate of diffusion directly, a series of comparative tests was performed in which  $D$  was determined for large and small grains at the same temperature. Four specimens were prepared by welding alloys A16 and B15 (Table 1); two of these were heated to 1100°C. for  $\frac{1}{2}$  hr. to develop large grains and then were annealed for diffusion at 800°C. for 330 hr. and 213 hr., respectively (tests 13 and 14, Table 2), with correction made for the diffusion that had occurred at 1100°C.; the other two specimens were given diffusion anneals of 227 hr. and 200 hr., respectively (tests 11 and 12, Table 2). The austenite grain sizes developed in these specimens are given in Table 2. The  $D$  values, at 0.54 wt. per cent C and at 800°C. for a specimen with 20 to 40 grains per square millimeter, was found to be  $0.31 \times 10^{-7}$  cm.<sup>2</sup> per sec. while for a specimen with 1000 to 2500 grains per square millimeter was  $0.36 \times 10^{-7}$  cm.<sup>2</sup> per sec.; at 0.7 per cent C the corresponding values were 0.35 and  $0.38 \times 10^{-7}$  cm.<sup>2</sup> per sec. Check tests (Tables 2 and 4; tests 12 and 13) were made and comparable  $D$  values averaged; these averages show that grain size has no appreciable effect upon  $D$ . It will be remembered that similar results have been reported for hydrogen and nitrogen.<sup>1</sup> Microscopic study showed that the number of grains per square millimeter in each of the two alloys making the specimen (A16 and



B15) did not vary materially from the weld zone to the end of the specimen (Figs. 10 and 11).

*Effect of Impurities.*—No variation in  $D$  values could be detected with change in the atmosphere in which the diffusion-anneal was performed, though the length of these anneals was such as to guarantee some gain or

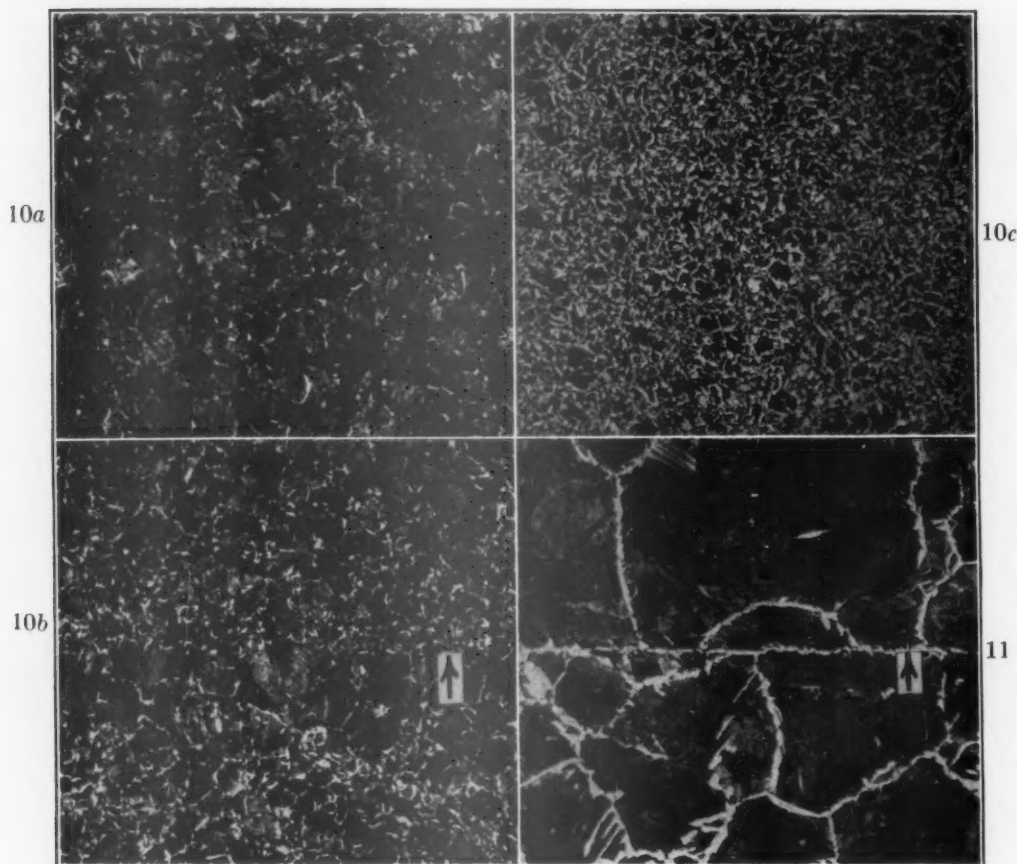


FIG. 10.—ALLOY B15, 0.80 PER CENT CARBON, WELDED TO A16, 0.43 PER CENT CARBON.  $\times 100$ .

Heated at 800°C. for 200 hours (test 12). Etched with nital. Arrow indicates position of weld. Shows a fairly uniform and small grain size throughout (10a, alloy B15; 10b, weld zone; and 10c, alloy A16).

FIG. 11.—ALLOY B15 WELDED TO A16.

Heated at 1100°C. for  $\frac{1}{2}$  hour, cooled to and held at 800°C. for 310 hours (Test 14). Etched with nital. Arrow indicates position of weld. Considerable grain growth occurred between 800° and 1100°C. (Compare Fig. 10b with Fig. 11.)

loss of gas.\* The  $D$  values at 1000°C. in tests 6, 9 and 10 (Table 4) at 0.1 and 0.7 wt. per cent C are essentially the same, though in test 6 the atmosphere was hydrogen, in test 9 vacuum, and in test 10 argon; at 0.1 wt. per cent C the values lay between  $2.6$  and  $3.0 \times 10^{-7}$  cm.<sup>2</sup> per sec., and at 0.7 wt. per cent C between  $3.2$  and  $3.3 \times 10^{-7}$  cm.<sup>2</sup> per sec.

\* W. R. Ham states that the specimens used should be practically saturated with hydrogen after  $\frac{1}{2}$  hr. at the diffusion-anneal temperature (private communication).



The plot of  $\log_{10} D$  against  $1/T$  for plain carbon steels showed all points to be close to a straight line even though the separate points were obtained from alloys differing widely in amounts of impurity (Fig. 12). This strongly suggests that the impurities present did not appreciably affect the  $D$  values in any case; the impurities present in these samples varied from 0.005 to 0.039 per cent P, 0.001 to 0.036 S, 0.005 to 0.27 Si, 0.005 to 0.85 Mn, 0.006 to 0.132 Cu, 0.003 to 0.08 O, and 0.002 to 0.005 N.

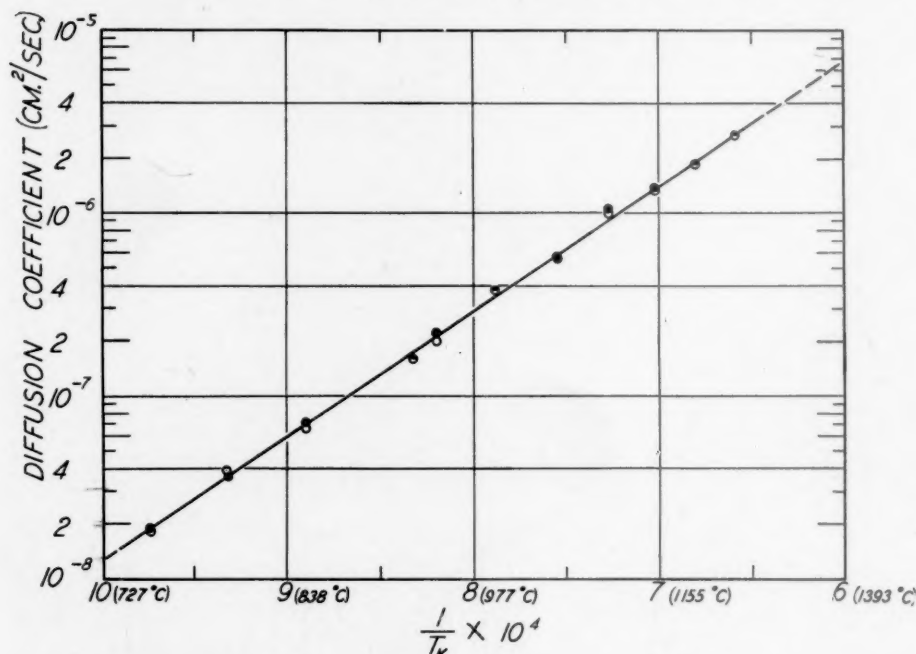


FIG. 12.—PLOT OF DIFFUSION COEFFICIENT  $D$  (LOGARITHMIC SCALE) AGAINST  $1/T$  ( $T$  IN DEGREES KELVIN).

$D$  values calculated by Grube method (open circles) and by Matano method (closed circles); half open circles represent coincident values. Concentration 0.70 weight per cent carbon (3.18 atomic per cent carbon).

Direct comparison of high-purity and commercial alloys confirmed these indirect results. Tests 7 and 8 represent such a comparison; specimen 7 consisted of alloys A4 and B7 (Table 1), which were high-purity iron and high-purity steel, respectively (A4 contained 0.04 per cent Ni and B7 0.03 per cent Si); specimen 8 consisted of alloys A5 and B3, which were commercial alloys and both were aluminum-killed. The  $D$  values calculated at 0.8 and 2.2 at. per cent C were found to be identical within experimental error. These were  $3.5$  and  $3.3 \times 10^{-7} \text{ cm}^2$  per sec. at 2.2 at. per cent and  $2.5$  and  $2.3 \times 10^{-7} \text{ cm}^2$  per sec. at 0.8 at. per cent C. Apparently an increase in sulphur from 0.001 to 0.03 per cent, silicon from 0.003 to 0.029 per cent, aluminum from less than a spectroscopic trace to a definite but unknown amount, manganese from 0.005 to 0.37 per cent, does not change the rate of diffusion of carbon to a detectable degree. A comparison of tests 8 and 33 shows that an increase of silicon from

0.05 to 0.25 per cent and manganese from 0.4 to 2.0 per cent likewise has no effect; in these tests the respective  $D$  values at 1.4 at. per cent C were 3.0 and  $2.7 \times 10^{-7}$  cm.<sup>2</sup> per sec.

*Effect of Oxygen.*—A comparison of tests 35 and 36 (Table 4) shows that oxygen dissolved in gamma iron, even to saturation, does not

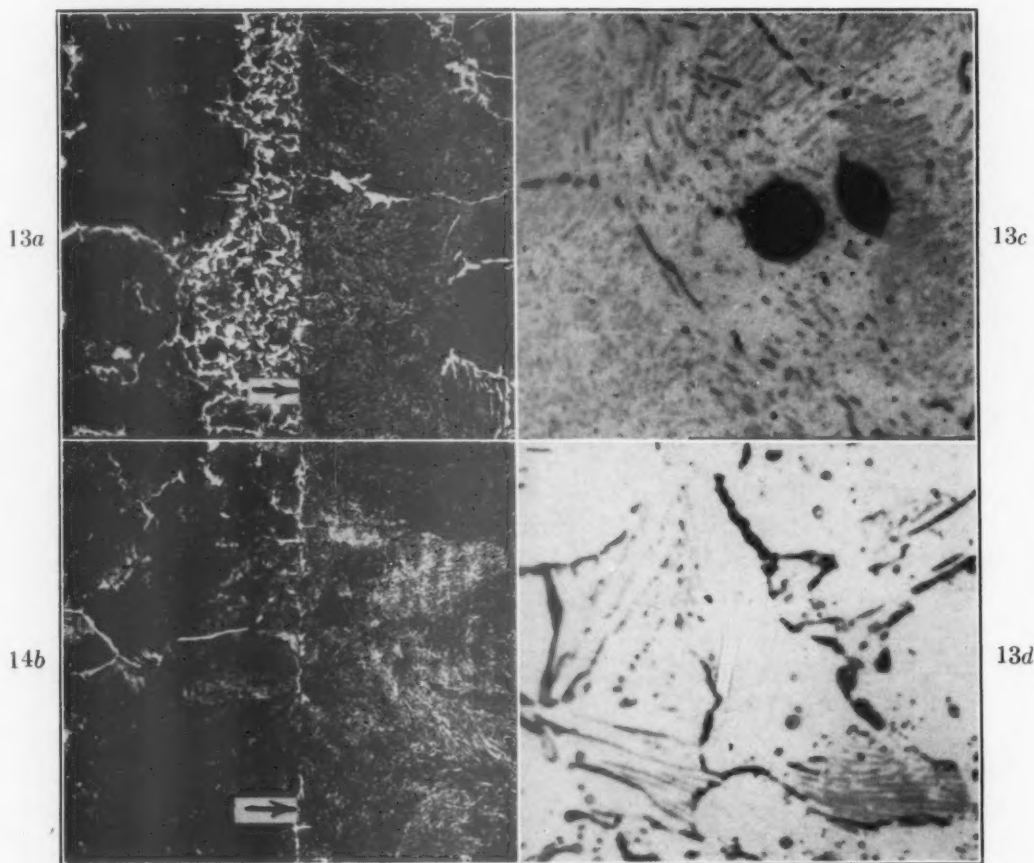


FIG. 13 (*a*, *c*, and *d*).—ALLOY B3, 1.07 PER CENT CARBON, WELDED TO A23, 0.006 PER CENT CARBON, 0.19 PER CENT OXYGEN (TEST 35).

FIG. 14*b*.—ALLOY B3 WAS WELDED TO A24, 0.03 PER CENT CARBON, 0.003 PER CENT OXYGEN (TEST 36).

Arrows indicate position of weld. Specimens were similarly treated (24 and 26½ hours at 1000°C.); etched with nital (*a* and *b*) and with sodium picrate (*c* and *d*). Magnifications 100 (*a* and *b*) and 2000 (*c* and *d*).

Shows: (1) iron oxide particles in A23 to persist in presence of high carbon (see *a* and *c*), and (2) internal oxidation in alloy B3 (13*a*, left) tending to inhibit austenite grain growth (compare 13*a* and 14*b*) and to render the structure of the cooled alloy somewhat abnormal (Fig. 13*d*).

appreciably change the rate of diffusion of carbon. Specimen 35 consisted of alloys B3 and A23; the impurity present in both alloys was relatively low except for 0.4 per cent Mn in B3 and 0.19 per cent oxygen in A23 (Table 1). Specimen 36 consisted of B3 and A24; the latter contained 0.003 per cent oxygen and small amounts of other elements. The calculated  $D$  values at 1000°C. were identical within experimental

limits. The values are at a concentration of 1.35 at. per cent carbon,  $2.6 \times 10^{-7}$  cm.<sup>2</sup> per sec. and  $2.8 \times 10^{-7}$  cm.<sup>2</sup> per sec., respectively. Evidence that the austenite of alloy A23 remained saturated with respect to oxygen during the annealing period is given in Fig. 13A and Fig. 13C. The effect of oxygen diffusing into alloy B3 on the grain size and microstructure is shown in Figs. 13A and 14B.

*Effect of Graphite.*—Tests 15 and 16 (Fig. 15) show that carbon in austenite diffuses at the same rate irrespective of whether the source of carbon is graphitic carbon or cementite. Prior to annealing the carbon in specimen 15 was present almost entirely as graphite, and in 16 as cementite. Except for this, both specimens were identical in all respects; both were annealed at the same temperature, 925°C. (Table 2).

*Effect of Manganese.*—The effect on  $D$  of an increase of manganese up to 2.5 per cent is negligible. At a carbon concentration of 0.5 wt. per cent (2.3 at. per cent) the rate of diffusion of carbon at 1000°C. was found to be  $3.3 \times 10^{-7}$  cm.<sup>2</sup> per sec. in a high-purity iron-carbon specimen containing less than 0.005 per cent Mn, and  $3.4 \times 10^{-7}$  cm.<sup>2</sup> per sec. in a high-purity iron-carbon-manganese specimen containing about 2.5 per cent Mn.

Results showing the influence of 16 per cent Mn on the rate of diffusion of carbon at any carbon concentration in the range between about 0 and 6 at. per cent C are given in Fig. 9. At low carbon concentrations the influence is small, but becomes more appreciable with increase of concentration. At about 6 at. per cent C (1.3 wt. per cent), 16 per cent of manganese increases the  $D$  value at 1000°C. from about 5.0 to  $7.0 \times 10^{-7}$  cm.<sup>2</sup> per sec.

*Effect of Nickel.*—Up to about 2 per cent, the effect of nickel in steel on the rate of diffusion of carbon is negligible. At a carbon concentration of 0.54 wt. per cent (2.43 at. per cent) the  $D$  value at 1000°C. in a plain carbon steel was found to be  $3.2 \times 10^{-7}$  cm.<sup>2</sup> per sec. (test 8, Table 4), and  $3.5^* \times 10^{-7}$  cm.<sup>2</sup> per sec. in a specimen containing 1.9 per cent Ni (test 29).

The effect of 20 per cent Ni on  $D$  over a range of carbon concentration between 0 and 3 at. per cent C is given in Fig. 9. At 3 at. per cent C (0.65 wt. per cent) the rate of diffusion of carbon in austenite at 1000°C. is increased from about  $3.6 \times 10^{-7}$  cm.<sup>2</sup> per sec. in a plain carbon steel to  $4.6 \times 10^{-7}$  cm.<sup>2</sup> per sec. in a 20 per cent Ni steel.

Apparently 20 per cent Ni and 16 per cent Mn have about the same effect on  $D$ , and in both cases the effect becomes more pronounced at higher carbon concentrations.

*Determination of  $Q$  and  $A$ .*—The effect of temperature upon the rate of diffusion may be represented by an exponential equation of the

\* Listed in Table 4,  $D$  at 1005°C. =  $3.8 \times 10^{-7}$  cm.<sup>2</sup> per sec. At 1000°C.  $D$  would be  $3.5 \times 10^{-7}$  cm.<sup>2</sup> per sec.

form  $D = A \cdot e^{-Q/RT}$ , where  $A$  is a constant,  $R$  the gas constant,  $T$  the absolute temperature and  $Q$  a constant familiarly known as the activation heat of diffusion.<sup>1</sup> In logarithmic form:  $\ln D = \ln A - Q/RT$ , the

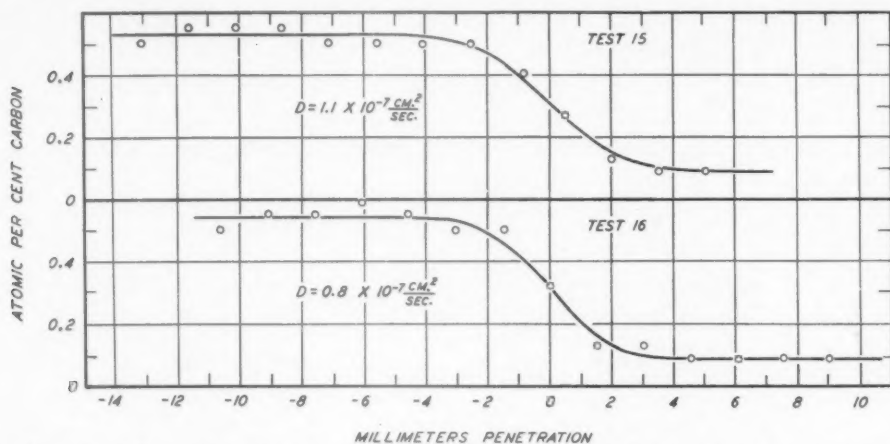


FIG. 15.—CURVES SHOWING THAT A CHANGE IN SOURCE OF CARBON (GRAPHITE IN TEST 15 AND CEMENTITE IN 16) HAS PRACTICALLY NO EFFECT ON RATE OF DIFFUSION OF CARBON IN THE GAMMA PHASE OF LOW-CARBON STEEL.

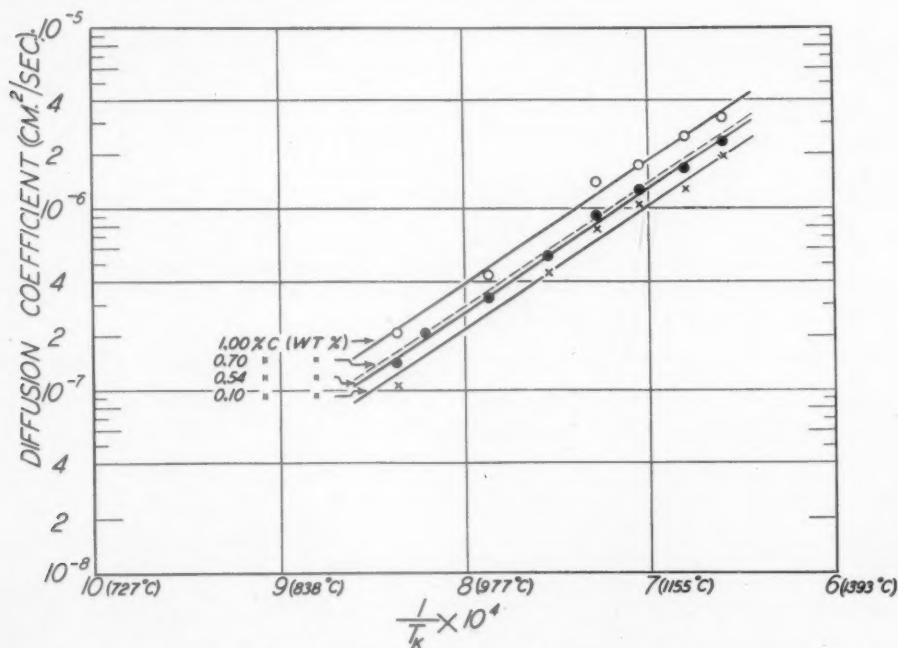


FIG. 16.—PLOT OF DIFFUSION COEFFICIENT (LOGARITHMIC SCALE) AGAINST  $1/T$  ( $T$  IN DEGREES KELVIN) AT VARIOUS CARBON CONCENTRATIONS.

Open circles, 1.00 per cent carbon; closed circles, 0.54 per cent carbon; and crosses, 0.10 per cent carbon.

equation gives a straight line when  $\ln D$  is plotted against  $1/T$ , for which  $Q/R$  is the slope. All data on diffusion in metallic systems are in conformity with this expression;<sup>1</sup> the data reported in this paper are likewise in conformity. Fig. 12 is a plot of  $\log_{10} D$  against  $1/T$  for the carbon



concentration 0.7 wt. per cent C, covering a temperature range of 500°C.; the slope of this curve, when correction is made to natural logarithms gives  $Q/R$ , which, multiplied by  $R$ , gives  $Q$ .<sup>1,19</sup>

Fig. 16 gives a series of plots for various carbon concentrations between 0.1 and 1.0 wt. per cent C; the slopes of these curves are identical within experimental error, signifying that the  $Q$  value,  $32,000 \pm 1000$  gram-calories, does not vary with carbon concentration with experimental error. Taking the Dushman-Langmuir equation

$$D = \frac{Q}{Nh} \cdot \delta^2 \cdot e^{-Q/RT}$$

where  $N$  is Avogadro's number,  $h$  is Plank's constant, and  $\delta$  the nearest approach of atoms, and employing the  $D$  values at 1000°C. for the con-

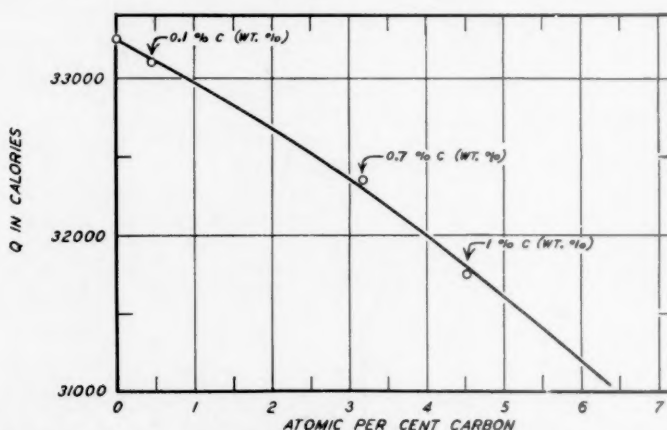


FIG. 17.—RELATION BETWEEN  $Q$  AND CARBON CONCENTRATION.

$Q$  values were calculated by Dushman-Langmuir equation.  $Q$  (activation heat of diffusion) is given in gram-calories per gram atom.

centrations 0.1 and 0.7 and 1.0 wt. per cent C, a calculation of the small variation in  $Q$  with concentration may be made. The following values were selected:  $D = 2.6 \times 10^{-7}$  cm.<sup>2</sup> per sec. at 0.1 per cent C,  $3.5 \times 10^{-7}$  cm.<sup>2</sup> per sec. at 0.7 per cent C,  $4.4 \times 10^{-7}$  cm.<sup>2</sup> per sec. at 1.0 per cent C,  $\delta = 1.826$  Å. at 0.1 per cent C, 1.837 Å. at 0.7 per cent C, 1.842 Å. at 1.0 per cent C. The nearest approach of atoms, the so-called diffusion "jump-distance," was assumed to be  $a_0/2$ ; values of  $a_0$ , the edge length of the unit face-centered cube of austenite, were taken from the data of Esser and Mueller.<sup>21</sup> Fig. 17 is a plot of the results of these calculations. This shows a slight decrease in  $Q$  with increase in carbon concentration. The agreement between the  $Q$  values calculated by the Dushman-Langmuir equation and those determined graphically from the  $\log D$  vs.  $1/T$  plots is excellent. At 0.7 wt. per cent C, where the  $D$  values are good probably to  $\pm 5$  per cent, the  $Q$  value determined from the  $\log D$  vs.  $1/T$  plot is 32,000 gram-cal., and that calculated from the Dushman-Langmuir equation is 32,350 gram-cal. One would not expect the



agreement to be so good at low and high carbon concentrations; at 0.1 wt. per cent C the  $Q$  value from the plot is 32,000 gram-cal., while that calculated from the Dushman-Langmuir equation is 33,100 gram-cal.; corresponding values at 1.0 wt. per cent C are 32,000 and 31,750 gram-cal., but this latter good agreement is believed to be accidental.

With values now available for  $D$  at various temperatures and concentrations and for  $Q$  at various concentrations, the constant  $A$  in the diffusion equation may be calculated. As stated above, the values of  $D$  may be taken as correct within  $\pm 5$  per cent at a concentration of 0.7 wt. per cent C and  $\pm 10$  per cent at the concentrations 0.1 and 1.0 wt. per cent C, while the values of  $Q$  may be taken as correct to within  $\pm 1.5$  per cent at 0.7 wt. per cent C and within  $\pm 3$  per cent at 0.1 and 1.0 wt. per cent C. The limits in error in the value of  $Q$  have a much greater effect upon the calculated value of  $A$  than those in the value of  $D$ , as may be seen by inspection of the form of the diffusion equation. Taking experimentally determined values of  $D$  and several values of  $Q$  within the estimated range of error in  $Q$ , values of  $A$  may be calculated; for the concentration 0.7 wt. per cent C,  $A = 0.094$  cm.<sup>2</sup> per sec. when  $Q = 31,500$  cal., and  $A = 0.147$  cm.<sup>2</sup> per sec. when  $Q = 32,500$ ; at 0.1 and 1.0 wt. per cent C,  $A = 0.072$  cm.<sup>2</sup> per sec. when  $Q = 31,000$  cal., and  $A = 0.185$  cm.<sup>2</sup> per sec. when  $Q = 33,000$  cal.; at the average value  $Q = 32,000$  cal.,  $A = 0.116$  cm.<sup>2</sup> per second.

#### THE DIFFUSION EQUATION

Taking  $A = 0.12 \pm 0.07$  and  $Q$  as  $32,000 \pm 1000$  gram-cal., the diffusion equation may then be written:

$$D_C^{\gamma\text{Fe}} = 0.12 \pm 0.07 \cdot e^{-\frac{32,000 \pm 1000}{RT}}$$

where  $D_C^{\gamma\text{Fe}}$  is the diffusion coefficient of carbon in gamma iron, in centimeters squared per second; the values of  $A$ , 0.12, is in cm.<sup>2</sup> per sec.; the value of  $Q$ , 32,000 is in gram-calories per gram atom;  $R$  is the gas constant;  $T$  is the temperature in degrees Kelvin. As written this equation applies to the diffusion of carbon in gamma iron throughout the concentration range from 0.1 to 1.0 wt. per cent C. The equation may be written with greater precision for the concentration 0.7 wt. per cent C:

$$D_C^{\gamma\text{Fe}} = 0.12 \pm 0.03 \cdot e^{-\frac{32,000 \pm 500}{RT}}$$

The two equations above give average values for  $A$  and  $Q$  and therefore can be used to calculate only average values for  $D$ . An empirical equation can be derived from which  $D$  values can be calculated for any concentration and any temperature within the ranges studied.

If the  $A$  values at various concentrations were plotted against concentration and a straight line drawn through these scattering points (assuming  $Q$  constant), the equation of this curve is  $0.07 + 0.06 \times$  the wt. per cent of C. Introducing this for  $A$  we have

$$D_C^{\gamma\text{Fe}} = (0.07 + 0.06 \times \text{per cent C}) \cdot e^{-\frac{32,000}{RT}}$$

This equation will permit a calculation of  $D$  within  $\pm 10$  per cent.

### Discussion

The diffusion coefficients obtained by Runge,<sup>3</sup> Tammann and Schönert,<sup>4</sup> Bramley and Allen,<sup>13</sup> and Paschke and Hauttmann,<sup>15</sup> and

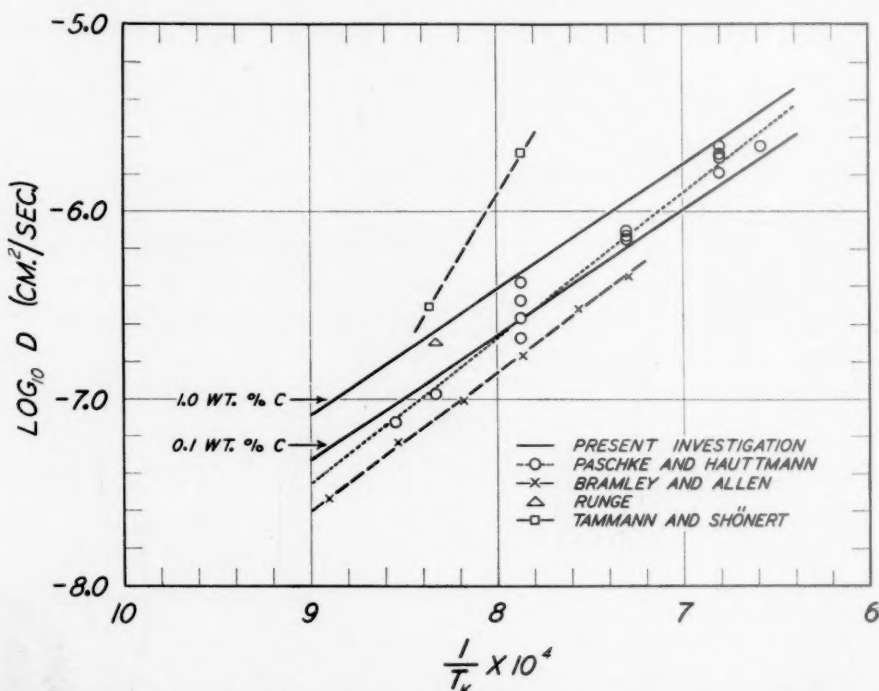


FIG. 18.—LOG  $D$  VERSUS  $1/T$  CURVES DETERMINED BY PASCHKE AND HAUTTMANN, BRAMLEY AND ALLEN, RUNGE, TAMMANN AND SCHÖNERT, AND BY WELLS AND MEHL.

those obtained in the present investigation are summarized in Fig. 18. Apart from those of the present work, these studies disregarded the influence of carbon concentration upon the rate of diffusion and accordingly the calculated  $D$  values must have suffered error from this source, which at a maximum can amount to 80 per cent. The data of Tammann and Schönert are doubtless the least accurate owing to the insensitive method employed to determine carbon concentration and to the uncertainty in the concentration of carbon on the surface of the specimen during carburizing. The data of Runge and 11 out of 14 of the points plotted from the data of Paschke and Hauttmann fall within the curves for 0.1 and 1.0 wt. per cent C; the latter points tend to fall more closely

to the lower curve than to the upper, owing probably to the fact that these workers used only those parts of the concentration-penetration curve lying between 0.03 and 0.53 wt. per cent C. If it is assumed that the data given by Paschke and Hauttmann may be taken to apply to a concentration of 0.25 wt. per cent C, about midway in the concentration range used, it may be observed that their data are in agreement with present data; at this concentration and at 1000°C. the respective  $D$  values are  $3.1 \times 10^{-7}$  cm.<sup>2</sup> per sec. and  $2.8 \times 10^{-7}$  cm.<sup>2</sup> per sec. The scatter of Paschke and Hauttmann's data is somewhat surprising, for the technique employed in the present work differs little from theirs.

The data of Bramley and Allen are low. If it is assumed that the carbon concentration at the surface of the specimen remains constant during either carburizing or decarburizing, and if it is further assumed that the gases present do not affect the value of  $D$  (a valid assumption on the basis of the results reported above), it should be possible to calculate  $D$  values accurately from carburizing or decarburizing experiments, provided that correct and pertinent solutions to Fick's law are used; as pointed out above, the solution to Fick's law used by Bramley and Allen is not pertinent. The assumption of a constant carbon concentration at the surface appears to be met by the carburizing experiment No. 25 of Bramley and Lawton,<sup>9</sup> after 5 hr. of carburizing Armco iron in a mixture of benzene vapor and carbon monoxide at 952°C. the surface carbon was 1.2 wt. per cent C, and after 80 hr. 1.3 wt. per cent C, both very near the saturation value at this temperature; the assumption appears to be met also by the decarburizing experiment No. 6 of Bramley and Allen,<sup>13</sup> in which a steel with 1.08 wt. per cent C was decarburized for 20 hr. at 1000°C. in a mixture of water vapor and hydrogen. The  $D$  values recalculated from the carburization data at 952°C. are as follows: at 0.1 wt. per cent C,  $1.6 \times 10^{-7}$ ; at 0.7 wt. per cent C,  $2.6 \times 10^{-7}$ ; at 1.0 wt. per cent C,  $2.9 \times 10^{-7}$  cm.<sup>2</sup> per sec.; comparable  $D$  values from the present work are 1.7, 2.1, and  $2.9 \times 10^{-7}$  cm.<sup>2</sup> per sec., respectively. The decarburization data furnish a value of  $D$  of  $2.1 \times 10^{-7}$  cm.<sup>2</sup> per sec. for a concentration of 0.3 wt. per cent C and a temperature of 1000°C. as compared to a value of  $2.8 \times 10^{-7}$  cm.<sup>2</sup> per sec. in the present work. Apparently, if either carburizing or decarburizing is continued for a sufficiently long time with the concentration of carbon at the surface known and remaining constant for, let us say, 90 per cent of the time,  $D$  values may be calculated from the concentration-penetration curve with good accuracy; obviously, then, the depth of carburizing or decarburizing may also be calculated from the  $D$  values as determined here when the same condition is met; if this condition is not met, only approximate and uncertain appraisals of depth can be made. It may be remarked that the close agreement of the  $D$  values calculated in this way with those determined in the present work confirm the observation

noted above that impurities in general, and oxygen and hydrogen in particular, affect the rate of diffusion of carbon only slightly, if at all.

Bramley<sup>6</sup> reports that nitrogen has no effect upon  $D$ , that oxygen and phosphorus decrease  $D$  slightly, and that sulphur decreases  $D$  markedly. The present results offer no information on the effect of nitrogen; in view of the inadequacies and indirectness in Bramley's work the reported effect of oxygen must be disputed on the basis of the present work; the amounts of sulphur to which Bramley referred were in the neighborhood of 0.5 per cent, which is far beyond those present in the steels studied here; and it may be concluded that the amount of sulphur present in commercial steel as impurity has no appreciable effect upon the rate of diffusion of carbon. Tammann and Schönert<sup>4</sup> report that impurities have a great effect upon  $D$ ; the inadequacies of experimental methods employed, however, appear to discredit this conclusion. It is interesting that the diffusion of carbon into iron containing relatively large amounts of oxygen is not attended by any evidence of reaction; this may be seen from the fact that the shape of the concentration-penetration curve is not altered by the presence of oxygen.

In previous work, the possible effects of grain size had been ignored, and in fact this effect is negligible. It has been shown that a change in grain size from less than one grain per square millimeter (less than A.S.T.M. No. -3) to more than 2000 grains per square millimeter (A.S.T.M. No. 8) has no appreciable effect on the rate of diffusion of carbon in gamma iron. This confirms the qualitative results of Mehl<sup>1</sup> and Rhines and Wells.<sup>23</sup>

Rowland and Upthegrove<sup>24</sup> found that large-grained steels decarburize between the  $A_1$  and  $A_3$  temperatures more rapidly than small-grained steels; this has been taken by some as evidence that carbon diffuses more rapidly in large grains of austenite than in small,<sup>25</sup> but the evidence is wholly indirect and of uncertain significance.<sup>23</sup>

The wholly negligible effect of alloying elements in the concentration ranges ordinarily obtaining in carburizing steels must be taken as proof that any difference in case depth produced by carburizing cannot have its origin in a different rate of diffusion of carbon (nor in minor differences in impurity, as these might be affected by the alloy addition). Data on the effect of case depth in dependence on alloy content are not very satisfactory. Any differences that might obtain must be ascribed to a difference in the surface concentrations of carbon as these are affected by particular alloy compositions.

It has generally been believed that the nature of austenite in plain carbon steels is independent of the source of carbon, whether cementite or graphite. Much discussion has centered around this question, however;<sup>18</sup> it has been suggested that the state of the solute carbon in austenite is different when the carbon originates from graphite than when it



originates from cementite. The present work offers no support for this point of view, for the diffusion coefficients are identical in the two cases. The sensitivity of diffusion coefficients to molecular and atomic states in solution constitutes this a powerful argument.<sup>1</sup>

The formation of pearlite from austenite requires the diffusion of carbon in gamma iron in order that the alternate layers of cementite and ferrite may form by segregation from homogeneous austenite. The rate of formation of pearlite depends on the rate of nucleation of pearlite and the rate of growth of pearlite nodules.<sup>26</sup> The rate of nucleation is probably related to the rate of diffusion of carbon, though in a manner not as yet understood. The rate of growth of pearlite nodules is determined by the rate of diffusion of carbon and the distance through which diffusion must occur; i.e., the interlamellar distance, as pointed out by Mehl.<sup>2</sup> Any alteration in either the rate of diffusion of carbon or in the interlamellar distance will alter the rate of growth of pearlite nodules, and thus the rate of formation of pearlite and ultimately the depth of hardening on quenching, since the rate of formation of pearlite determines this.

Since grain size has no effect upon the rate of diffusion, it may be concluded that any effect of grain size on the rate of growth of pearlite nodules cannot be caused by a difference in rate of diffusion; if such an effect exists, it must originate in a change in interlamellar spacing, which, though unlikely, has been stated to occur. In a similar fashion it may be argued that any effect upon the rate of growth of pearlite nodules by impurities or by alloying elements in moderate amounts cannot originate in an alteration in rate of diffusion of carbon. As stated earlier,<sup>1,2</sup> the effect of alloying elements (Ni, Mn, etc.) in retarding the rate of growth of pearlite nodules must originate in the inherently slower rates of diffusion of the alloying elements themselves, which also segregate when pearlite forms. The lack of effects of grain size, of impurities, and of small amounts of alloying elements on the rate of diffusion of carbon thus, fortunately, greatly simplifies the study of the rate of carburizing and of the rate of formation of pearlite.

#### SUMMARY

1. Concentration-penetration curves for the diffusion of carbon in gamma iron have been determined, by diffusing carbon from high-carbon into low-carbon alloys and by subsequent chemical analysis of layers, which upon calculation yield diffusion coefficients. The diffusion coefficient  $D$  has been determined in a temperature range of 750° to 1250°C. and in a concentration range of 0.1 to 1.0 weight per cent carbon. At 0.7 weight per cent carbon the  $D$  value is accurate within  $\pm 5$  per cent and at 0.1 and 1.0 weight per cent carbon within  $\pm 10$  per cent.



2. From the variation of  $D$  with temperature the activation heat of diffusion,  $Q$ , has been determined graphically. At 0.7 weight per cent carbon  $Q$  is  $32,000 \pm 500$  per gram-atomic weight; at 0.1 and 1.0 weight per cent carbon  $Q$  has the same value but the error is  $\pm 1000$  cal. These values are in accord with the Dushman-Langmuir equation.

3. For the range from 0.1 to 1.0 weight per cent carbon, the diffusion equation is:

$$D_C^{\gamma\text{Fe}} = 0.12 \pm 0.07 \cdot e^{-\frac{32,000 \pm 1000}{RT}}$$

This is an average equation which does not give the variation in  $D$  with concentration. At 0.7 weight per cent carbon the constants are more precise:

$$D_C^{\gamma\text{Fe}} = 0.12 \pm 0.03 \cdot e^{-\frac{32,000 \pm 500}{RT}}$$

4. The rate of diffusion increases with increasing carbon concentration by approximately 80 per cent between 0.1 and 1.0 weight per cent carbon. This increase is approximately independent of temperature.  $D$  values in a temperature range between  $750^\circ$  and  $1250^\circ\text{C}$ . and a composition range of 0.1 to 1.0 weight per cent carbon can be calculated within  $\pm 10$  per cent from the empirical equation

$$D_C^{\gamma\text{Fe}} = (0.07 + 0.06 \times \text{per cent C}) \cdot e^{-\frac{32,000}{RT}}$$

5. The rate of diffusion does not vary with grain size in the range of A.S.T.M. No. -3 to A.S.T.M. No. 8, within the experimental error given.

6. The rate of diffusion does not vary with impurities ordinarily present in commercial steels, within the experimental error given; no effect upon  $D$  obtains when oxygen is as high as 0.19 weight per cent.

7. Manganese and nickel, up to 20 weight per cent, increase the rate of diffusion, but this increase is inappreciable for the amounts of these elements ordinarily present in heat-treating or carburizing steels.

8. The significance of these results for the study of the carburizing process and for study of the formation of pearlite from austenite is discussed.

#### ACKNOWLEDGMENTS

The authors wish to thank C. H. Herty, Jr., of the Bethlehem Steel Co., W. J. Reagan, of the Edgewater Steel Co., J. L. Holmquist, of the Spang-Chalfant Division, National Supply Co., V. N. Krivobok, of the Allegheny Ludlum Steel Corporation, N. B. Pilling, of the International Nickel Co., A. B. Beeken of the Vulcan Crucible Steel Co., John Chipman, of the Massachusetts Institute of Technology, and other friends in the steel industry for supplying materials and the hundreds of

chemical analyses used in the determination of concentration-penetration curves. In addition, the authors appreciate the assistance given by Miss E. B. Pearsall and other members of the staff of the Metals Research Laboratory.

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## DISCUSSION

(John S. Marsh presiding)

E. C. SMITH,\* Cleveland, Ohio.—When handled in large production carburizing commercially there is no appreciable difference in case depth between fine-grained nickel steels and coarse-grained nickel steels. There is a tendency to confuse the lower hardening of the finer grained steels with case depth. The fine-grained steels are more difficult to harden, and this may be charged as due to producing shallow case depths.

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\* Chief Metallurgist, Republic Steel Corporation.

# Crystallography of Austenite Decomposition

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A.I.M.E.

(New York Meeting, February 1940)

METALLURGISTS have long believed that martensite in steel forms as plates along the octahedral {111} planes of austenite. Much has been written about mechanisms whereby units of the austenite lattice are pictured as transforming to martensite by shearing movements initiated along the octahedral planes of austenite, supposedly resulting in plates of martensite lying parallel to these planes of shear.

A critical inspection of two or three photomicrographs of quenched hypereutectoid steel led us to the conclusion that the orientation habit of martensite, at least in hypereutectoid austenite, could not possibly be octahedral. Inasmuch as recent studies<sup>30,31</sup> of the martensite-type reaction in nonferrous alloy systems have established the irrational orientation habit as characteristic of this type of lattice transformation, the need for a thorough restudy of the crystallography of martensite formation in steel was evident. The present paper reports the results of such a study, extended to include both cementite and some of the products of constant-temperature decomposition of austenite. Also reported are a few of the results obtained from a microscopic and X-ray study of the austempering process in very high-carbon steel.

## I. THE MARTENSITE TRANSFORMATION

### *Previous Work*

*Microstructure and Crystal Structure of Martensite.*—Among the best series of published photomicrographs of quenched steels are those of Whitely,<sup>1</sup> Robertson,<sup>2</sup> Hanemann and Schrader,<sup>3</sup> and Lucas.<sup>4</sup> The crystal structure of martensite is body-centered tetragonal, with axial ratio varying from 1 near 0.0 per cent carbon to 1.08 for 1.75 per cent

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Part of the material presented in this paper has been abstracted from a thesis submitted by A. R. Troiano in partial fulfillment of the requirements for the degree of Doctor of Science, Harvard University, June 1939. Manuscript received at the office of the Institute Nov. 1, 1939; revised Jan. 10, 1940. Issued as T.P. 1212 in METALS TECHNOLOGY, August 1940.

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<sup>30</sup> References are at the end of the paper.



carbon. Apparently, it is generally accepted that this axial ratio is a linear function of carbon content.<sup>5,6,7</sup> Each martensite plate is evidently a single crystal, which may or may not have a distorted crystallinity. Considerable interest has been centered about the midrib that is so characteristic of very high-carbon martensite but which can also be seen, though less distinctly, in martensite of eutectoid composition. Sauveur<sup>8</sup> suggested that in some instances the midrib might be troostite; Desch<sup>9</sup> considers it to be a sheet of cementite perhaps one molecule thick. Scheil<sup>10</sup> deformed a 29 per cent Ni steel (carbon content not stated) containing large well formed martensite needles and obtained cross markings (similar to slip lines in appearance) traversing the martensite needles; he concluded, therefore, that the midrib could not be a dividing line between two different martensite orientations, and admitted that a satisfactory explanation of the midrib was not available.

*Kinetics of Martensite Formation.*—Greninger and Troiano<sup>11</sup> have recently published the results of a microscopic study of the kinetics of

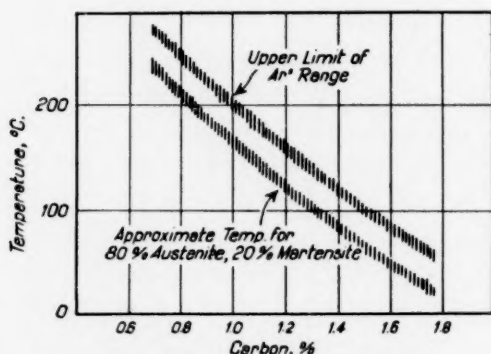


FIG. 1.—INFLUENCE OF COMPOSITION ON MARTENSITE TRANSFORMATION TEMPERATURE RANGE FOR PLAIN CARBON STEEL, AFTER GRENINGER AND TROIANO.<sup>11</sup>

martensite formation in plain carbon steels. In this paper are also summarized and contrasted the prominent interpretations that have been given to the martensite transformation, and the conclusion is made that the "S-curve" of Davenport and Bain<sup>12,13</sup> gives an incorrect picture of the martensite process; the curves are in error for all temperatures within the martensite range of iron-carbon alloys. The older concept (advanced, though never proved, by several earlier investigators\*), that martensite forms from austenite only during cooling through the proper temperature range, was found to be substantially correct. In Fig. 1 is reproduced Greninger and Troiano's  $Ar''$  curve, which for heat-treatments making use of the interrupted quench (the austempering treatment) shows the temperatures for the beginning of martensite formation as a function of carbon content.

*Mechanism of Martensite Formation.*—Mehl, Barrett, and Smith,<sup>15</sup> after a crystallographic study of 0.42, 0.86, and 1.3 per cent carbon steels, concluded that the martensite plates delineate the  $\{111\}$  planes of the parent austenite. Specimens of these steels were quenched in water after heating 2 hr. at 1100°C., and were then tempered 1 hr. at 200°C. to facilitate the microscopic examination. A frequency plot was made of

\* See, for example, the summary by Carpenter and Robertson, ref. 14.



martensite midrib traces on a single polished surface of each grain. Believing that the traces they had measured could be comprised in four groupings for each austenite crystal, they concluded that the orientation habit was octahedral, for only the {111} planes in a cubic crystal have a multiplicity of four. Apparently, the only other crystallographic study of the martensite orientation is that of Hanemann,<sup>16</sup> whose work appeared before that of Mehl, Barrett, and Smith. Hanemann's work was done on a quenched specimen of 1.52 per cent carbon steel having very large austenite grain size. He measured the location of martensite traces on two adjacent polished surfaces, and thus obtained values for the angles between the planes delineated by martensite plates. No attempt was made to evaluate the austenite grain orientation. Hanemann concluded that the martensite plates delineate both {111} and {100} planes of the austenite lattice.

The lattice relationships\* between austenite and martensite in carbon steels have been studied by Kurdjumow and Sachs,<sup>17</sup> and by Wassermann,<sup>18</sup> and in iron-nickel alloys by Nishiyama,<sup>19</sup> Wassermann,<sup>18</sup> and Mehl and Derge.<sup>20</sup>

### Experimental Methods

*Alloys and Specimen Size.*—The analyses of the steels employed are given in Table 1. Alloys 1 and 2 were supplied by Mr. G. V. Luers-

TABLE 1.—Percentage Composition of Steels Employed

Steel No.	C	Mn	Si	Cr	Ni
PLAIN CARBON STEELS					
1	1.78	0.18	0.15	0.12	0.10
2	1.40	0.01	0.06	0.02	0.03
3	0.92	0.22	0.03		
4	0.35				
NICKEL ALLOYS					
5	1.23				11.5
6					32.5

sen, of the Carpenter Steel Co.; No. 1 in the form of  $\frac{1}{4}$ -in. square rod and No. 2 in ingot form. Alloy 3 is a commercial steel, received in the form of  $\frac{3}{4}$ -in. dia. rod; metallographic specimens (for sizes see below) were taken from the center  $\frac{1}{4}$  in. of the rod to avoid decarburization effect. Alloy 4 is a high-purity alloy, prepared in a high-vacuum molybdenum-wound resistance furnace from carbonyl iron and sugar charcoal.

\* For a summary of results of lattice-relationship studies, see Mehl and Derge, ref. 20.

Alloys 5 and 6 are two of many nickel\* steels prepared in the high-vacuum furnace. In addition to the above, several high-purity iron-carbon alloys and commercial steels of various carbon contents were used in supplementary or corroborative experiments. Specimen sizes (except as otherwise noted) were as follows: The large specimens used for microscopic and orientation studies varied from about  $\frac{1}{4}$  by  $\frac{1}{4}$  by  $\frac{3}{16}$  in. to  $\frac{1}{4}$  by  $\frac{3}{8}$  by  $\frac{1}{2}$  in., the small specimens used for Debye X-ray patterns and for some of the microscopic studies were about  $\frac{1}{4}$  in. long and from 0.035 to 0.045 in. square in cross section.

*Orientation Determinations.*—All orientation data were plotted, and the solution arrived at, stereographically, with the aid of a 15 $\frac{3}{4}$ -in. dia. stereographic net.<sup>21</sup> Whenever possible, the austenite grain orientation was determined by means of the back-reflection Laue method;<sup>22</sup> the accuracy of these evaluations was within about  $\frac{1}{2}^\circ$ . This method was used for all the nickel steels and for the plain carbon steels containing 1.78 and 1.40 per cent carbon. The austenite grains in the quenched 1.78 per cent carbon steel were found to be free from any distortion, in so far as one may judge from the sharpness of back-reflection Laue spots. The austenite Laue spots from quenched 1.4 per cent carbon steel were about twice the size of those from 1.78 per cent carbon steel; for carbon contents below about 1.4 per cent (corresponding to increasing amounts of martensite present in a quenched specimen), the back-reflection Laue spots (if any) were so ill defined as to render the method unsuitable. For these lower carbon steels, a method based on the following was used for evaluating austenite grain orientation.

Almost all austenite grains contain one or more twin bands. Even though there may be no retained austenite in a specimen (for example, a 0.5 per cent carbon steel quenched to room temperature would be all martensite), *vestiges* of these twin bands may be seen in a large-grained sample if it is examined critically, after etching, with limited azimuth dark-field illumination at low magnifications. The identification of these twin-band vestiges is a particularly simple matter when the austenite is made to transform in such a way that the specimen contains at room temperature perhaps 20 per cent tempered martensite and the remaining martensite in the untempered condition. Large-grained (1 mm. or more) specimens having the desired heat-treatment were polished on two or three surfaces and searched for twin bands. In almost every specimen there was found at least one grain containing two or more suitable twins. A second surface of polish of the selected grain was prepared, and it was then possible to measure the location of two or more twin bands on two surfaces; these measurements thus provided the location of two  $\{111\}$  poles, and hence the orientation, of the austenite

\* Nickel used was Baker's analyzed nickle shot, of which the major impurity was iron.

grain with an accuracy at least equal to that of the back-reflection Laue method. The above method will be referred to hereinafter as the "method of twin-band vestiges."

### Results

*Microstructure of Martensite.*—The shape of martensite crystals varies with carbon content. At highest carbon contents, the martensite crystals are truly platelike, and on a polished surface are featured by: (1) the remarkably straight midrib and (2) the zig-zag grouping, wherein acute angles are formed between two midribs seemingly emanating from a point. This acute-angle feature (illustrated in Fig. 2*b*) is characteristic of martensite formed from austenite of 1.8 per cent carbon to about 1.5 per cent carbon. Near 1.4 per cent carbon, the shape of martensite crystals appears to undergo a sudden change; the acute angle is no longer present. Instead, two midribs emanating from a point characteristically form an obtuse angle, and the midrib is much less prominent than it is for carbon contents above about 1.5 per cent (Fig. 3). With decreasing carbon contents (below 1.4 per cent\*) martensite crystals gradually assume a lathlike shape. In eutectoid steel the ratio between the long and short dimensions of the lath varies considerably. For this carbon content, midribs are revealed only with difficulty.

*Martensite in 1.78 Per Cent Carbon Steel.*†—Specimens of steel No. 1 were heated for about ten minutes at 1250° to 1300°C. in inert atmosphere, then slowly cooled to 1150°C. or 1130°C. and quenched in a solution of 10 per cent NaOH. This treatment produced large (1 to 3 mm.) grains of austenite containing about 20 per cent martensite. Two surfaces of polish approximately at right angles were prepared on selected specimens and measurements of martensite midrib locations (Figs. 2*a* and 2*b*) were then made on the two surfaces of pertinent grains. Results are summarized in Fig. 5, which shows 21 poles obtained from 7 grains in 5 specimens.

In addition to the above, work was also carried out on a high-purity alloy of iron and carbon containing about 2 per cent carbon. Specimens quenched from 1130°C. (hence containing austenite of maximum carbon content, corresponding to point *E* of the equilibrium diagram) yielded martensite poles identical to those reported in Fig. 5 for 1.78 per cent carbon steel.

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\* Between carbon contents of about 1.3 and 0.6 per cent the shape of martensite crystals can properly be studied only on specimens that have been given a special type of heat-treatment. See the heat-treatment described in the following pages under "Martensite in 0.92 per cent Carbon Steel."

† The preliminary results from this study were announced in a letter to *Nature* (ref. 23).

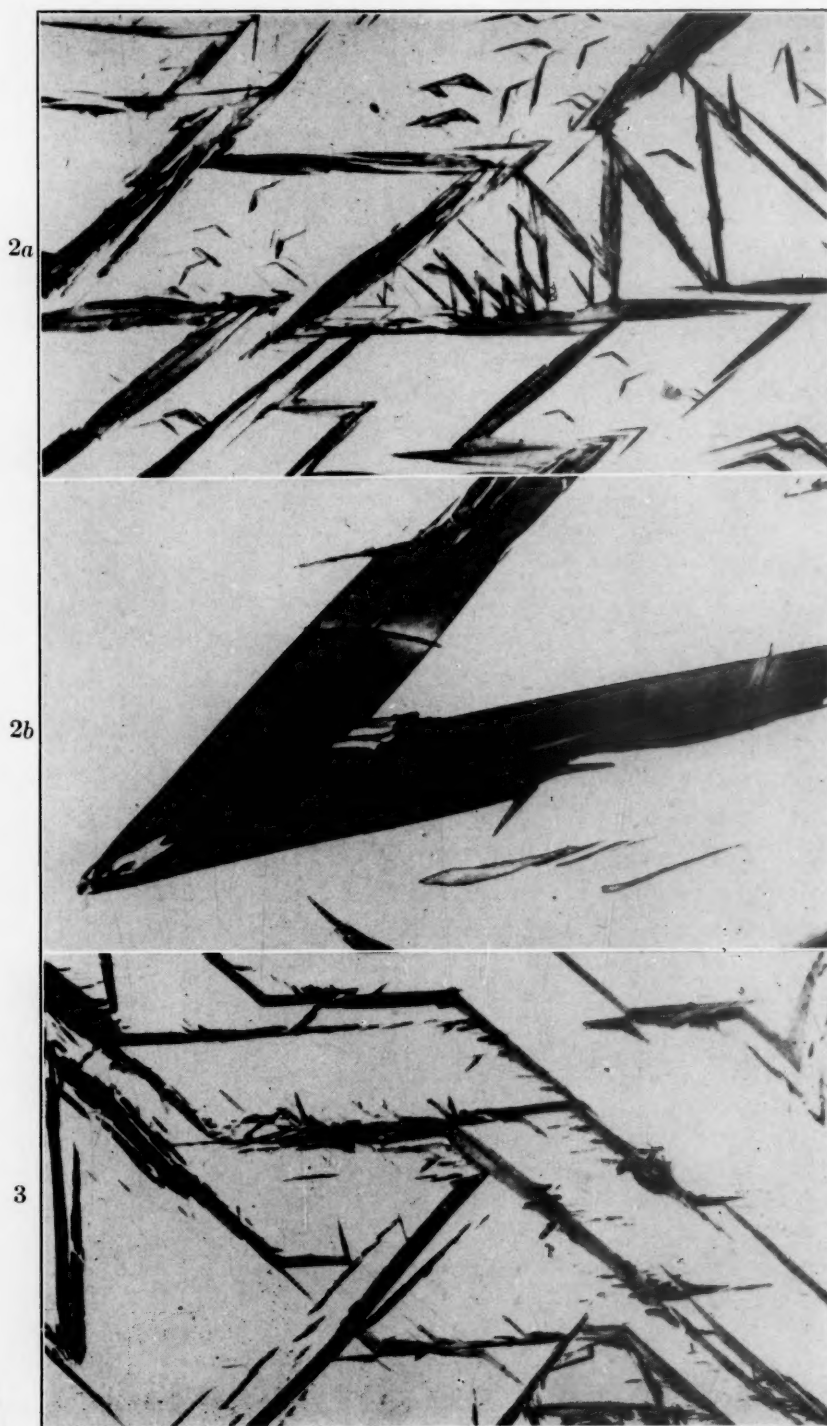


FIG. 2.—MARTENSITE AND AUSTENITE IN 1.78 PER CENT CARBON STEEL.

a. Polished, then tempered 10 sec. at  $200^{\circ}\text{C}$ ., repolished and photographed. Etched with Nital.  $\times 500$ .

b. Etched with Nital.  $\times 1000$ .

FIG. 3.—MARTENSITE FORMED BETWEEN  $120^{\circ}\text{C}$ . AND  $100^{\circ}\text{C}$ . IN 1.40 PER CENT CARBON STEEL.

Etched with Nital.  $\times 500$ . White background is a mixture of austenite and white martensite; see text for treatment details.



Rods of steel No. 1, as received, had a decarburized rim; the outer  $\frac{1}{16}$ -in. rim analyzed 1.61 per cent carbon. Grains lying on the extreme surface of this rod were also studied (single-surface work, hence trace normals, not poles, were measured) and the habit of these martensite midribs was again found to be the same as that reported in Fig. 5 for 1.78 per cent carbon steel.

Thus, it is certain that for plain carbon steels, in the range of carbon content between 1.8 and about 1.5 per cent, the orientation habit of martensite in austenite remains the same. As may be seen in Fig. 5, the martensite plates are not parallel to any low-indices plane of austenite;

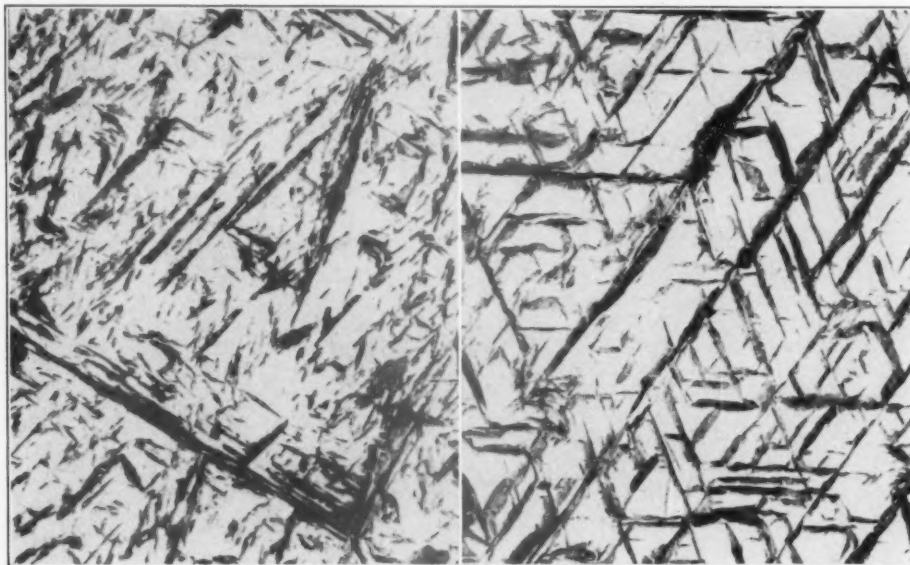


FIG. 4.—MARTENSITE FORMED BETWEEN ABOUT 220° AND 180°C. IN 0.92 PER CENT CARBON STEEL. ETCHED WITH NITAL.  $\times 500$ .

a. White background is a mixture of austenite and white martensite. See text for treatment details.

b. Another area of specimen of Fig. a.  $\times 500$ .

the center of the stereographic region of austenite delineated by the martensite poles lies about  $3^\circ$  from  $\{124\}_\gamma$  and may be described  $\pm 1^\circ$  as  $\{4\ 10\ 18\}$  of the austenite lattice.

*Martensite in 1.40 Per Cent Carbon Steel.*—Two types of heat-treatment were used in this study. One specimen of steel No. 2 was heated for 30 min. in argon at  $1400^\circ\text{C}$ . and was then slowly cooled to  $1100^\circ\text{C}$ . and quenched into a metal bath held at  $100^\circ\text{C}$ . The specimen remained in this bath for 10 sec. and was then rapidly transferred to a tempering bath held at  $250^\circ\text{C}$ ., where it remained for 5 sec. (the latter treatment tempered the martensite that had formed during the cooling from about  $120^\circ$  to  $100^\circ\text{C}$ .; see Fig. 3); the specimen was then quenched to room temperature in 10 per cent NaOH. A second specimen of steel No. 2



was quenched from 1150°C. into a metal bath held at 150°C., and the metal bath containing the specimen was allowed to cool from 150° to 110°C. over a period of 15 min.; the specimen was then removed, tempered rapidly at 200°C., and quenched to room temperature in 10 per cent NaOH.

In both of the above specimens, complete orientation studies\* were

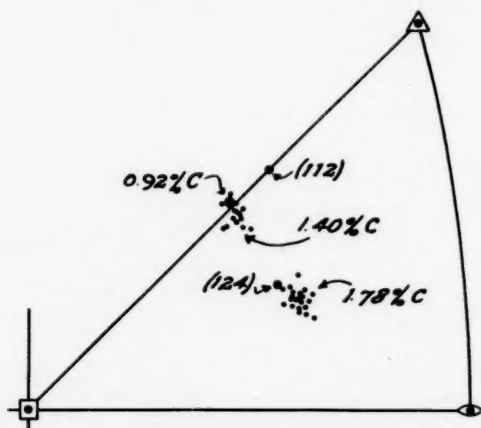


FIG. 5.—STEREOGRAPHIC PROJECTION OF MARTENSITE POLES IN 1.78, 1.40, AND 0.92 PER CENT CARBON STEEL.

Because of space limitations, poles from 0.92 per cent carbon steel are plotted in an adjoining triangle. All trace normals for 0.92 per cent carbon martensite passed through shaded area.

confined to the tempered martensite. Microscopic study showed the midribs in the untempered martensite, revealed after long etching, to be accurately parallel to those of the tempered martensite. In the second specimen, this tempered martensite had formed during very slow cooling, whereas in the first specimen it had formed during comparatively rapid cooling. The results obtained from the two specimens were the same, and are summarized in Fig. 5, which shows 14 poles taken from 3 grains. These martensite poles are located about 10° from the 1.78 per cent carbon martensite poles; the multiplicity is now 12 instead of 24.

The center of the stereographic region delineated by the 1.40 per cent carbon martensite poles may be described  $\pm 1^\circ$  as  $\{4\ 4\ 10\}$  of the austenite lattice.

**Martensite in 0.92 Per Cent Carbon Steel.**—A specimen of steel No. 3 was heated for 80 min. in inert atmosphere at 1350°C., then slowly cooled to 950°C. and quenched into a liquid metal bath held at 180°C. The specimen remained in this bath for 15 sec.; it was then rapidly transferred to a second metal bath held at 250°C. (to temper the martensite that had formed during cooling from about 220° to 180°C.), and after remaining 15 sec. in the tempering bath it was quenched to room temperature in a solution of 10 per cent NaOH. The orientations of selected grains (size about 5 mm.) were evaluated by the method of twin-band vestiges.†

As already mentioned, the shape of martensite crystals in steel of near-eutectoid composition tends to be lathlike (Fig. 4), and crystals for which accurate measurements of traces on two surfaces can be made are

\* Procedure was the same as for the 1.78 per cent carbon steel.

† See description under "Experimental Methods."

not common. Only two satisfactory poles were located for the grain studied (Fig. 5). However, eight good trace normals were measured on one surface of the particular grain, and all of these eight lines passed within a degree of the stereographic region delineated by the two poles. As may be seen in Fig. 5, the orientation habit of 0.92 per cent carbon martensite is the same as that of 1.40 per cent carbon martensite.

The long dimension of the martensite crystals is accurately parallel to  $\langle 110 \rangle$  of the austenite lattice. This solution was arrived at by studying grains in which long dimensions were contained in the surface of polish; these directions were related to austenite zones by the usual stereographic methods. Because this long dimension of martensite crystals coincides with  $\langle 110 \rangle$  of the austenite lattice, an austenite grain whose surface of polish is within a few degrees of being parallel to  $\{111\}$  will in certain regions contain a seemingly unique grouping of martensite crystals (Fig. 4b), wherein the long dimensions correspond to the three  $\langle 110 \rangle$  directions in an octahedral plane.

*Martensite in Hypoeutectoid Steel.*—From a critical inspection of martensite crystals in a 0.70 per cent carbon high-purity steel and a 0.55 per cent carbon commercial steel (using the quench-and-temper technique described above), the conclusion was drawn that the habit of these must be very similar to, and probably is the same as, that evaluated for 0.92 per cent carbon. However, at some carbon content below 0.55 per cent the mechanism of martensite formation apparently undergoes a change, and possibly it is advisable to withhold comment upon this change until the hypoeutectoid steels shall have been studied as thoroughly as have been the hypereutectoid steels described above. A single experiment performed on a 0.35 per cent carbon steel yielded results in agreement with those reported by Mehl, Barrett, and Smith.<sup>15</sup> That is, in a low carbon steel the platelike array of martensite "striations"\* is parallel to  $\{111\}$  of the austenite lattice.

*Martensite in High-carbon Nickel Steel.*—Phragmén<sup>24</sup> has made a brief study of the orientation habit of martensite in an alloy steel containing 12 per cent nickel and 1 per cent carbon. He carried the work only far enough to show that the martensite habit was definitely not octahedral, as had been supposed; and he stated that his results were at least consistent with those of Greninger and Troiano<sup>23</sup> on plain carbon steel.

Steel No. 5 after furnace cooling from the melt was found to consist of austenite (grain size 10 mm. or larger) plus precipitated carbide. Specimens cut from the ingot were heated for 12 min. at 1100°C. in nitrogen and then quenched to room temperature in water. After this treatment, the specimen was all austenite (no recrystallization took

\* For a good photomicrograph of low-carbon martensite see ref. 3.

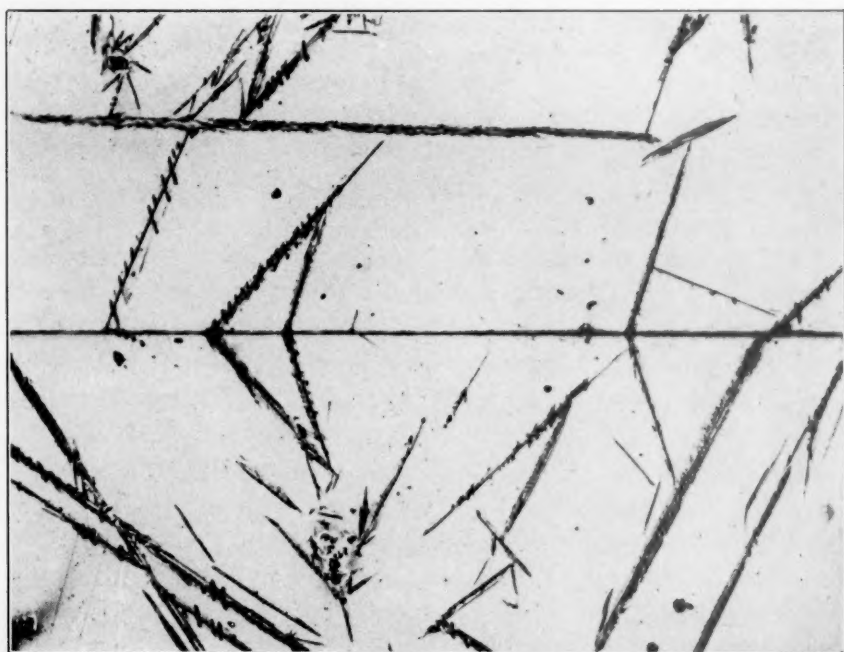


FIG. 6.—MARTENSITE IN AN ALLOY OF 11.5 PER CENT NICKEL AND 1.23 PER CENT CARBON.

Formed by cooling austenite to  $-77^{\circ}\text{C}$ . Tempered 10 minutes at  $100^{\circ}\text{C}$ . Composite photomicrograph of two surfaces at right angles. Etched with Nital.  $\times 150$ .

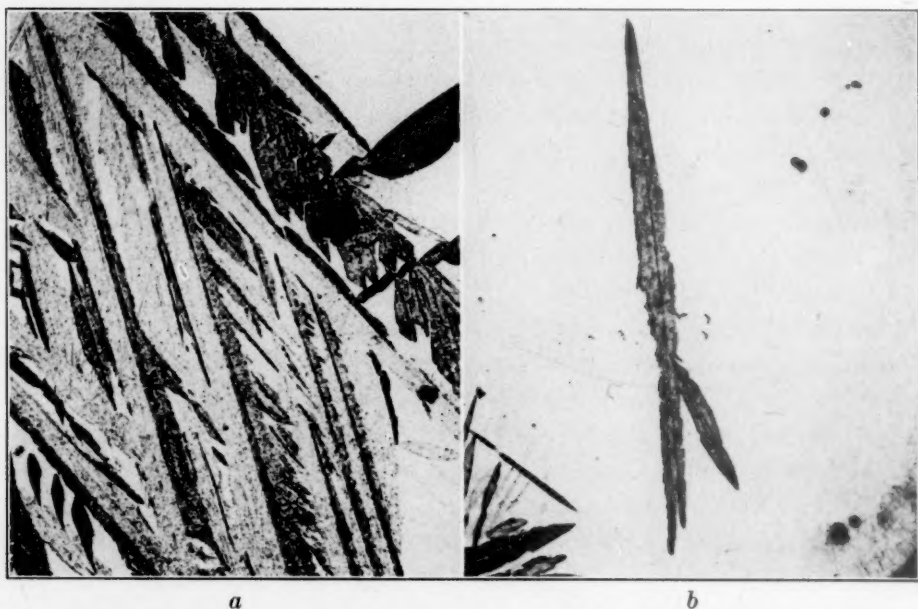


FIG. 7.—MARTENSITE IN AN ALLOY OF IRON PLUS 32.5 PER CENT NICKEL, FORMED BY COOLING AUSTENITE TO  $-77^{\circ}\text{C}$ .  $\times 150$ .

*a.* Etched with a saturated solution of ferric chloride in water, acidified with hydrochloric acid and diluted 1:4 with alcohol. White background is austenite.

*b.* Another area of specimen of Fig. 7*a*.

place during the heating). The specimen was then dipped into a mixture of carbon dioxide and acetone ( $-77^{\circ}\text{C}.$ ), which caused the formation of about 5 per cent white martensite. The specimen was then tempered for 10 min. at  $100^{\circ}\text{C}.$  to facilitate subsequent microscopic examination (Fig. 6). The orientation habit of the martensite was then evaluated, following the same procedure as that for the 1.78 per cent carbon steel, with results as shown in Fig. 8. As may be seen, the orientation habit of this martensite is, except for scatter, the same as that of martensite in plain carbon steel containing 1.78 per cent carbon.

*Martensite in an Alloy of Iron*

*and Nickel.*—From a preliminary metallographic study of a series of high-purity alloys of iron and nickel, it was established that certain compositions will form a martensite that greatly resembles that of high-carbon steel (Fig. 7); the crystal structure of this iron-nickel martensite is body-centered cubic instead of tetragonal.\* The following orientation studies have been carried out on this structure.

Alloy No. 6 (32.5 per cent Ni) after slow cooling from the melt was all austenite at room temperature, with a grain size of about 30 mm. Specimens of this ingot after dipping into a mixture of carbon dioxide and acetone ( $-77^{\circ}\text{C}.$ ) contained about 5 per cent martensite. Austenite grain orientation was first evaluated by the back-reflection Laue method; the specimen was polished and then cooled to  $-77^{\circ}\text{C}.$ , after which the measurements of midrib location were made without etching the specimen. The specimen was then repolished and cooled to  $-192^{\circ}\text{C}.$  (in liquid air), and the orientation of the martensite formed in the lower temperature range was also determined. As may be seen in Fig. 8, the orientation habit of the martensite formed by cooling to  $-77^{\circ}\text{C}.$  is the same as that of the martensite formed by cooling from  $-77^{\circ}$  to  $-192^{\circ}\text{C}.$  Again, no important crystallographic planes of austenite are delineated by the martensite plates. The orientation habit is only slightly different from that of 1.78 per cent carbon martensite; hence the transformation mechanisms for these two alloys must be nearly the same, in spite of the fact that one contains large amounts of carbon, the other none.

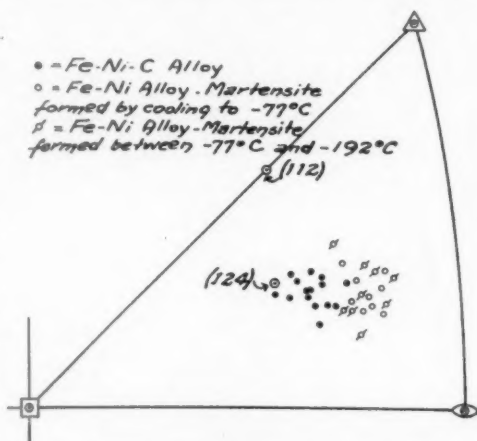


FIG. 8.—STEREOGRAPHIC PROJECTION OF MARTENSITE POLES IN NICKEL STEELS.

\* For alloy steel as well as plain carbon steel, the axial ratio of martensite is apparently a function of carbon content only. See ref. 25.



## II. TRANSFORMATION OF HYPEREUTECTOID AUSTENITE ON CONTINUOUS COOLING

Two points are of immediate interest in connection with the transformation of hypereutectoid austenite on quenching at rates lower than the critical cooling velocity: One concerns the shape and orientation of cementite precipitated during this cooling, and the other has to do with the influence of this slow cooling on the process and result of the martensite transformation. There has been no adequate study of microstructures resulting from this heat-treatment. Mehl, Barrett and Smith<sup>15</sup> have studied the orientation habit of cementite in cast steel containing 1.3 per cent carbon; they found that the cementite poles cover a rather wide area on the unit stereographic triangle of austenite, and that the cementite plate has a limited fiber structure, with [100] as fiber axis. In 1930, Wever and Engel<sup>26</sup> reported low values for the martensite axial ratio in a 1.28 per cent carbon steel obtained from specimens quenched at rates below the critical cooling velocity; their results for this steel are summarized below:

COOLING VELOCITY, DEG. C. PER SEC.	AXIAL RATIO
3,000	1.047
890	1.040
317	1.028

Wever and Engel interpreted these results as indicating that the axial ratio of martensite is a function of cooling velocity. These results and conclusions have been taken to be confirmation of the theory of Esser and co-workers,<sup>27,28</sup> which pictures the tetragonality of martensite as caused by a distortion of the lattice on quenching; the lower the temperature of Ar," the greater the distortion or tetragonality.

### *Martensite Axial Ratio and Cooling Velocity*

Specimens of 1.78 per cent carbon steel about  $\frac{1}{4}$  by  $\frac{1}{4}$  by  $\frac{3}{16}$  in. in size were heated 10 min. at 1250°C. in nitrogen; slowly cooled to 1150°C., and quenched into warm water held at various temperatures between 40° and 100°C. Microscopic examination revealed that for quenching-bath temperatures of 60°C. or below, the normal austenite-plus-martensite structure characteristic of steel of this carbon content was obtained; and for quenching-bath temperatures of 95° and 100°C. the microstructure was nodular troostite plus cementite plates. Intermediate quenching-bath temperatures yielded microstructures similar to those illustrated in Figs. 9, 10, and 11, which show a matrix of austenite containing cementite plates surrounded by martensite. Thus, there is a certain narrow range of cooling velocities that allows the formation of



cementite and no primary troostite, and at some later stage of the cooling process, martensite forms pseudomorphically about the cementite plates.

Small specimens (size,  $\frac{1}{4}$  in. long and 0.035 to 0.045 in. square in cross section) were also quenched in the manner outlined above, and



FIG. 9.—1.78 PER CENT CARBON STEEL QUENCHED FROM 1150°C. INTO HOT WATER AT 85°C.  $\times 200$ .

Etched with Nital. Austenite matrix containing cementite surrounded by pseudomorphous martensite.

FIG. 10.—ANOTHER AREA OF SPECIMEN IN FIG. 9.  $\times 200$ .

FIG. 11.—ANOTHER AREA OF SPECIMEN IN FIG. 9.  $\times 2300$ .

examined microscopically. Debye X-ray patterns (cobalt radiation, filtered) obtained from small specimens having a microstructure like that shown in Figs. 9 to 11 exhibited the following features: the presence of well defined  $\text{Fe}_2\text{C}$  lines, a normal austenite parameter, and a sub-normal martensite axial ratio. In general, the lower the cooling veloc-

ity, the lower was the axial ratio of the martensite.\* For example, a specimen quenched in water at 80°C. yielded an austenite parameter of 3.622 Å. and a martensite axial ratio of 1.048, whereas the normal martensite axial ratio for this steel is 1.080.

Wever and Engel's<sup>26</sup> subnormal axial ratios for martensite are thus readily explained. The subnormal values are not due to any direct dependence of martensite axial ratio upon cooling velocity, as has been claimed by Esser and Engelhardt.<sup>28</sup> Rather, they are due to the fact that in specimens given this heat-treatment, martensite forms in austenite regions depleted in carbon content by cementite precipitation. These comparatively low-carbon regions adjacent to the cementite plates will have a higher  $Ar''$  range than is normal† for this steel; hence, on cooling, martensite will form first in these regions and only when there has been very little cementite precipitated will there be formed any martensite of normal appearance and normal axial ratio.

#### *Orientation Habit of Cementite‡ Formed at $Ar'$*

The orientation habit of cementite was studied in specimens of 1.78 per cent carbon steel. Specimens quenched from 1130°C. in boiling water, hence containing cementite plus primary troostite, yielded results§ practically identical with those of Mehl, Barrett and Smith.<sup>15</sup> It will be noticed from Figs. 9 to 11 that the traces of cementite plates are occasionally very straight, even at highest magnification. A plate whose trace on one surface is long and straight will normally have a second-surface trace that is rather short and wavy. This long straight direction contained in a cementite plate may be likened to the long dimension of a lath or to an axis of limited fibering; and, in fact, Mehl, Barrett, and Smith<sup>15</sup> have shown that a cementite plate is really a limited fiber aggregate in which the crystallites scatter  $\pm 10^\circ$  about the [100] zone axis. This straight direction of cementite was related to the austenite lattice in the following manner: Polished and etched specimens containing austenite, cementite and pseudomorphic martensite were

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\* The use of hot water for quenching does not result in reproducible conditions, and results tended to be somewhat erratic. That is, the structures shown in Figs. 9, 10 and 11 were sometimes obtained for 80° water and at other times for 60° water. Mainly for this reason, the small specimens were always examined microscopically before they were used for Debye patterns.

† See Fig. 1.

‡ According to the results of recent dilatometric studies by Wever and Rose,<sup>29</sup> the temperature of  $A_{cm}$  is markedly influenced by cooling rates, and for a cooling velocity of 15°C. per second,  $A_{cm}$  is completely suppressed and cementite precipitation becomes a part of the  $Ar'$  transformation. See ref. 29, Fig. 12.

§ Austenite grain orientation was determined by a combination of the method of twin-band vestiges and optical study of oriented sheen.

searched for straight cementite traces.\* The orientations of grains containing these traces were then determined by means of the back-reflection Laue method, and direction-cosines were evaluated stereographically. Twenty-two separate measurements were made in three grains and the average of these gave an approximate direction in the austenite lattice of  $\langle 134 \rangle$ . Details of measurements are given in Table 2.

TABLE 2.—*Measurements of Angles between Crystallographic Axes of Austenite and Fiber Axis of Cementite*  
DEGREES

Grain No. 1			Grain No. 2			Grain No. 3		
$\alpha$	$\beta$	$\gamma$	$\alpha$	$\beta$	$\gamma$	$\alpha$	$\beta$	$\gamma$
37.5	54	86	42	49	80.5	43	44	84
43.5	48	81.5	44	51	71.5	31	59	71.5
42.5	49	86	39	64.5	68.5	36	56	78
33	57	86.5	41.5	49	87	38	60.5	81
37	46	77	41.5	44	84			
38	46.5	64	21	72	74			
36	58	76	48	51	67			
36	55	82	29	57	78.5			
32	62	78	13	74	80			
AVERAGE ANGLE								
37.3	52.8	79.7	35.5	56.8	76.8	36.5	54.9	78.6
COSINE								
0.79	0.61	0.19	0.81	0.55	0.23	0.80	0.58	0.20

$$\text{Weighted average from three grains} \left\{ \begin{array}{l} \cos \alpha = 0.80 \\ \cos \beta = 0.58 \\ \cos \gamma = 0.21 \end{array} \right.$$

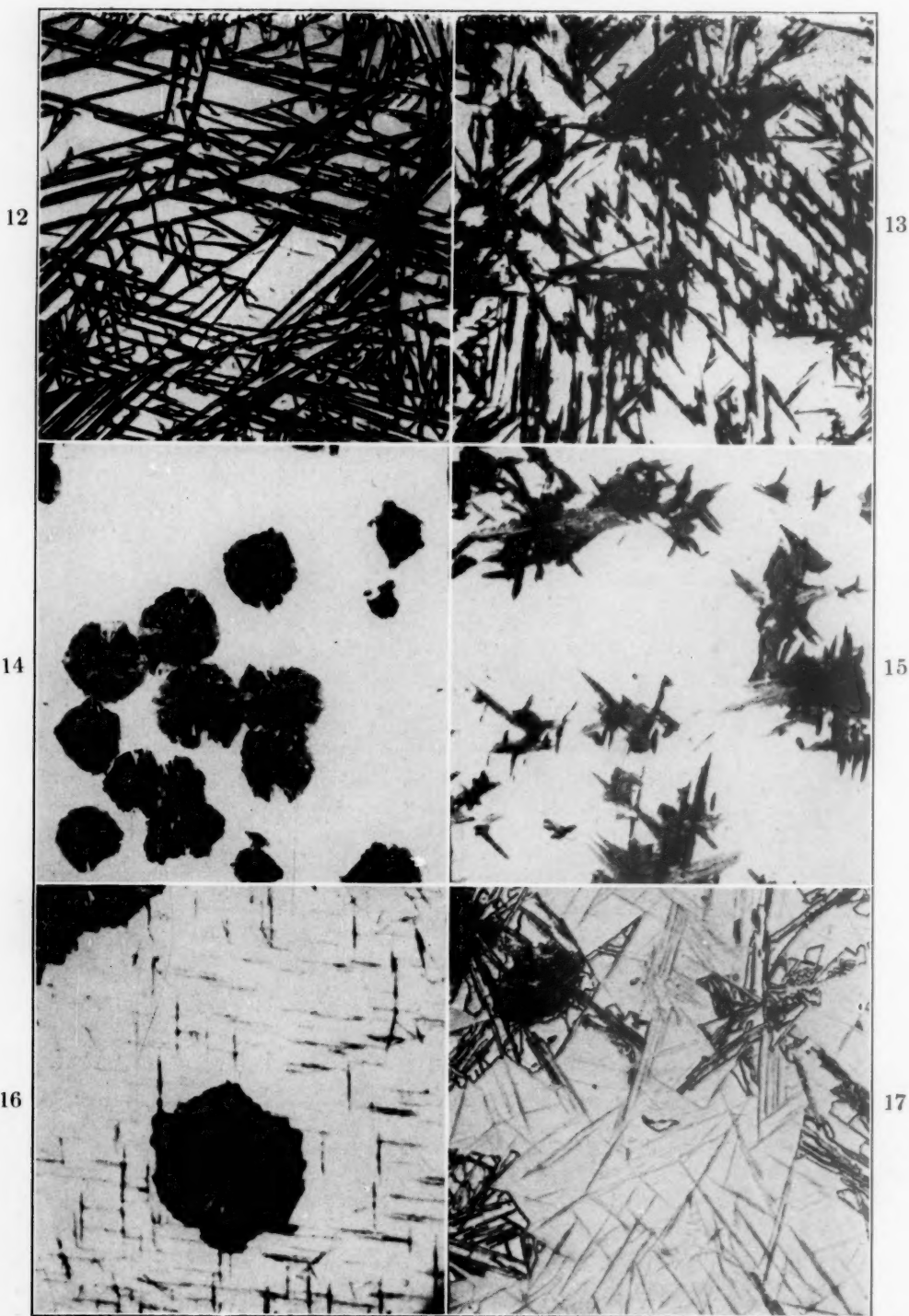
$$\text{Approximate ratio} = [uvw] = 431$$

### III. TRANSFORMATION OF AUSTENITE AT CONSTANT SUBCRITICAL TEMPERATURES

#### *Austempering Structures in 1.78 Per Cent Carbon Steel*

*Microscopic and X-ray Studies.*—Specimens of 1.78 per cent carbon steel slightly smaller than  $\frac{1}{4}$  by  $\frac{1}{4}$  by  $\frac{3}{16}$  in. were heated 10 min. in argon at 1250°C., slowly cooled to 1150°C., and quenched in liquid metal baths held at various temperatures between 100° and 710°C.; at measured intervals of time, specimens were removed from the austempering bath and quenched to room temperature in 10 per cent NaOH and then exam-

\* The criterion of "straightness" was the ability to repeat measurements on parallel traces to within  $\frac{1}{4}^\circ$ .



FIGS. 12-17.—1.78 PER CENT CARBON STEEL QUENCHED FROM 1150°C. INTO LIQUID METAL BATHS, AND AUSTEMPERED FOR TIMES AND AT TEMPERATURES INDICATED. ALL  $\times 500$ .

Etched in Nital. Time given is total time of immersion and not necessarily time at temperature. See text for details.

Fig. 12, 100°C., 100 days.

Fig. 13, 200°C., 41 hours.

Fig. 14, 300°C., 35 minutes.

Fig. 15, 450°C., 10 seconds.

Fig. 16, 550°C., 3 seconds.

Fig. 17, 710°C., 5 minutes.



ined microscopically. It was found impossible to attain critical cooling velocities by quenching specimens of the size used into metal baths held at temperatures above 300°C.; small amounts of cementite precipitated at grain boundaries. For these higher austempering temperatures, the procedure followed was first to quench into a metal bath at 100°C.,\* then rapidly to transfer the specimen to the austempering bath. The austempering structures for this steel are illustrated in Figs. 12 to 17.

The 100°C. product appears in the form of well defined plates that bear little or no resemblance to martensite, either tempered or untempered, of this carbon content.† The first visible decomposition at this temperature appears after about three days, in the form of very fine black lines. With increasing times, new lines appear and the lines become thicker. For times of less than about 50 days, white martensite is present in specimens after quenching to room temperature. As times increase from 3 to 50 days, the amount of 100°C. product increases and the amount of white martensite decreases; the 50-day specimen contains practically no martensite.

The 200°C. product also is in the form of plates; the structure is easily differentiated from both martensite and the 100° product, though the grouping of plates bears some resemblance to the zig-zag grouping of martensite. The plates are more irregular and less defined than those produced at 100°C. At 225°C. the plates are irregular and the first evidences of a nodular type of reaction may be seen. For increasing temperatures, the nodular reaction is more and more predominant, and the 300°C. decomposition results in the well formed nodules illustrated in Fig. 14.‡ These nodules increase in size with time just as do the nodules of primary troostite. For temperatures above 300°C., the nodules become less prominent, and the product again gradually assumes a platelike shape, which is fairly well developed at 450°C. At 550°C., the product is again nodular (primary troostite); cementite plates also form at this temperature. For temperatures above the range of maximum transformation rate, the decomposition process consists of two parts: (1) rapid precipitation of cementite, and (2) slow decomposition of the remaining austenite into cementite and alpha iron—the pearlite reaction. At 710°C., cementite formation is practically instantaneous, and the remaining austenite begins to transform after 4 min. at temperature.

X-ray diffraction studies were carried out on small specimens ( $\frac{1}{4}$  in. long and 0.035 to 0.045 in. square in cross section) heated 3 min. in argon

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\* For this steel the upper limit of the Ar'' range is 65°C.

† Compare Fig. 2.

‡ An identical structure is obtained in 1.40 per cent carbon steel when austenite decomposes at 350°C. (but not at 300°C.). Thus, for both steels nodules result from decomposition at a temperature of about 250°C. above Ar''.



at 1150°C. and austempered at various temperatures. Pertinent observations that can be made are: (1) For all temperatures below the "knee" of the "S-curve," the austempering process results in no change in the lattice parameter of austenite. As long as the austenite diffraction lines were measurable, the lattice parameter remained constant at  $3.621 \text{ \AA.} \pm 0.001 \text{ \AA.}$  (2) Above the "knee" of the "S-curve," decomposition is first homogeneous (cementite formation) and then heterogeneous (pearlite reaction). A specimen austempered  $2\frac{1}{2}$  sec. at 710°C. had an austenite

parameter of  $3.584 \text{ \AA.}$  and a martensite axial ratio of 1.043 (both of these values correspond about to eutectoid composition), and the pattern contained well defined cementite lines.

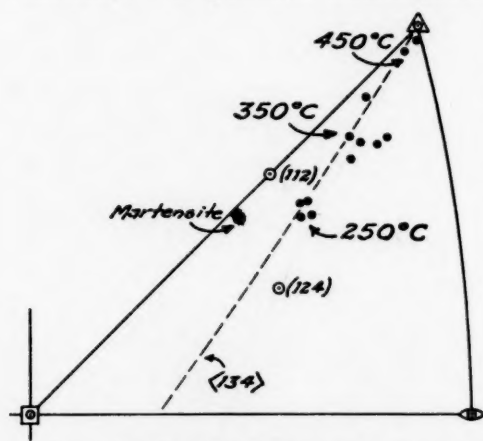


FIG. 18.—STEREOGRAPHIC PROJECTION OF POLES OF AUSTEMPERING PRODUCTS IN 1.78 PER CENT CARBON STEEL.

Plotted in one stereographic triangle of the austenite lattice. Shaded area is region delineated by martensite poles.

region delineated by martensite poles for this steel. The poles of the 100°C product lie about 15° from those of the 200° product, and these two stereographic regions\* are each separated by about 7° from the poles of martensite (which forms on cooling from 65°C. to room temperature).

*Orientation Habits of the 100°C. and 200°C. Products.*—The orientation habits of both the 100°C. and the 200°C. austempering products in 1.78 per cent carbon steel have been evaluated; for the former, a 212-hr. specimen was used, and for the latter a 41-hr. specimen. Results are summarized in Fig. 18, which also shows, for purposes of comparison, the stereographic

#### *Austempering Structures in 0.92 Per Cent Carbon Steel*

The product of the austempering process in 0.92 per cent carbon steel is platelike, in varying degrees of perfection, for all temperatures between the martensite range and the temperature range that produces primary troostite. Photomicrographs illustrating these structures are shown in Figs. 19 to 21. The orientation habits of the 250°, 350°, and 450° products are described below, and results are summarized in Fig. 22. All specimens were heated 1 hr. in nitrogen at 1350°C. and were quenched

\* It is certain that much of this scatter, particularly for the 100°C. product, is experimental; and is due to the fact that, with reference to  $\times 500$  magnification, the production of a flat surface at an edge is practically impossible. If the need should arise, these regions could be located more accurately by means of careful trace-normal work away from the edge of a grain.

from 950°C. Austenite orientations were determined by the method of twin-band vestiges.

In addition to the four accurately located poles of the 250° product (Fig. 22), 19 trace normals were located and all of these trace normals passed through the stereographic region limited by the four poles of

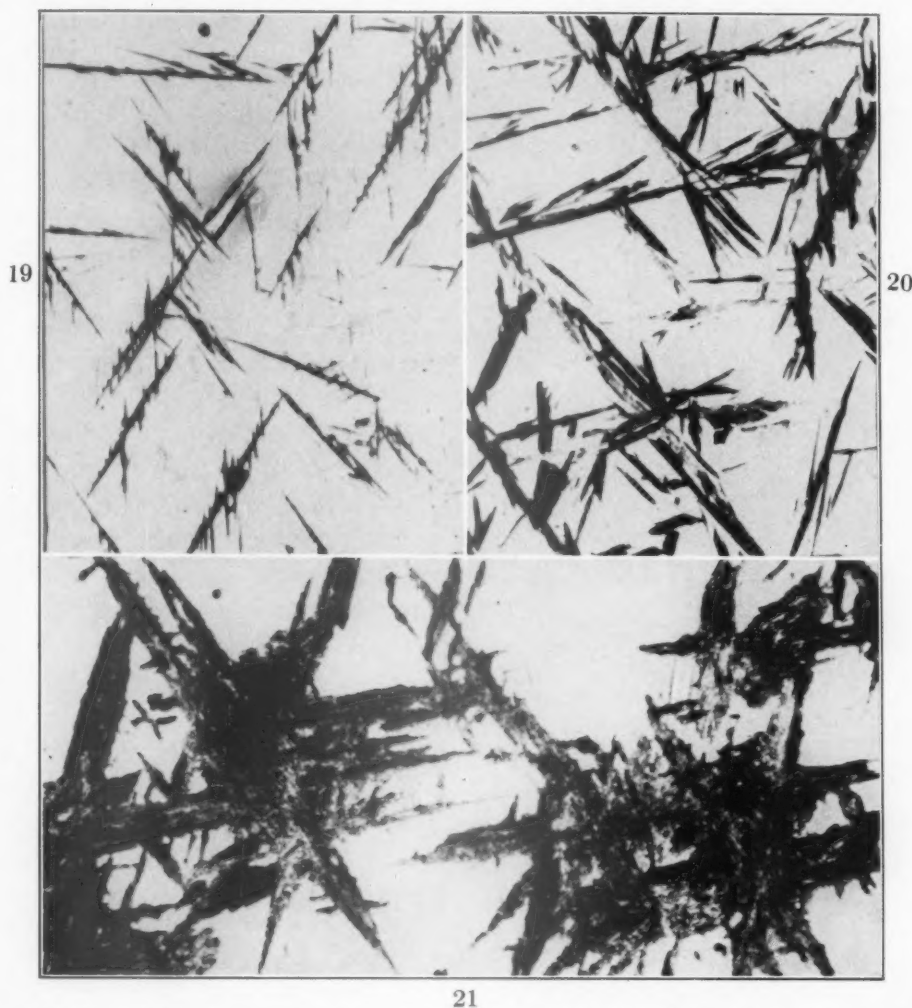


FIG. 19-21.—0.92 PER CENT CARBON STEEL AUSTEMPERED FOR TIMES AND AT TEMPERATURES INDICATED.  $\times 500$ . ETCHED IN NITAL.

Fig. 19, 250°C., 10 minutes.

Fig. 20, 350°C., 90 seconds.

Fig. 21, 450°C., 35 seconds.

Fig. 22. This region is separated 7° from the region delineated by martensite poles in this steel. The plates of the 350°C. product have more scatter in orientation habit than have those of the 250°C. product; trace-normal measurements proved this scatter to be real, not experimental. The increase in decomposition temperature from 250° to 350°C. results in a displacement of pole position of about 9° in the direction toward the

octahedral pole of the stereographic triangle. Only two poles of the 450°C. product are shown; it was deemed unnecessary to locate more, for the orientation habit of this product is definitely close to octahedral.

### DISCUSSION

It has been definitely proved that the orientation habit of martensite is not octahedral, as had been previously assumed. In none of the alloys studied, except the 0.35 per cent carbon steel, does a martensite plate delineate a low-indices plane of austenite; it is admitted that the martensite transformation in low-carbon steel is in some ways different from that

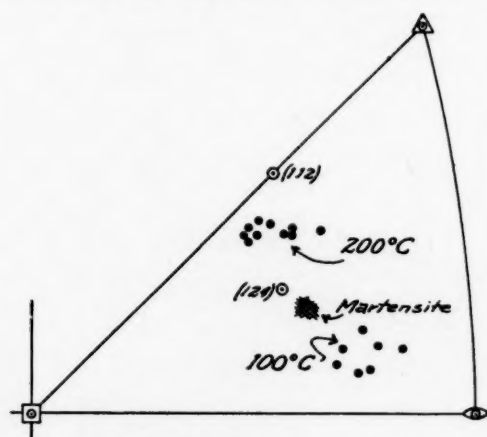


FIG. 22.—STEREOGRAPHIC PROJECTION OF POLES OF AUSTEMPERING PRODUCTS IN 0.92 PER CENT CARBON STEEL, PLOTTED IN ONE STEREOGRAPHIC TRIANGLE OF THE AUSTENITE LATTICE. SHADED AREA IS REGION DELINEATED BY MARTENSITE POLES.

in high-carbon steel. The orientation habits are of very high indices, and in this respect the results agree with those of previous studies of martensite structures in copper-zinc,<sup>30</sup> copper-tin,<sup>30</sup> and copper-aluminum<sup>31</sup> alloys. A new point has developed from the study of iron-carbon martensite: The orientation habit changes rather abruptly at about 1.4 per cent carbon, and this is accompanied by a corresponding change in microstructure or shape of the martensite crystal. Presumably, there are no other abrupt changes in the curves for properties vs. carbon content at this composition;\* certainly there is no abrupt change in crystal structure. This can mean only that factors other than crystal structures are important in determining the orientation habit of a martensite lattice; hence, an explanation of "irrational" habit must await the naming and the study of these other variables.

It has been shown that midribs are a prominent structural feature of martensite crystals formed at low temperatures in high-purity iron-nickel alloys.† This fact obviates any role that carbon, or proeutectoid cementite as suggested by Mehl,<sup>34</sup> might play in the formation of the midrib.

Phragmén,<sup>24</sup> in attempting to correlate the irrationality of martensite habit with the transformation mechanism of Kurdjumow and Sachs,<sup>17</sup> has considered the possibility that the glide planes of shear (the octa-

\* In his rather detailed microscopic study of the Ar'' curve for plain carbon steels, Hanemann<sup>32</sup> calls attention to a change in slope of the curve at a carbon content of 1.4 per cent.

† See also photographs by Wyman,<sup>33</sup> which show martensite midribs in iron-cobalt-nickel alloys.

hedral planes) of the latter mechanism may function even though they are not parallel to the martensite plates. This possibility he dismisses as inconsistent with the almost perfect parallelism of martensite plates and their high speed of formation. Considering these and other inconsistencies, the whole picture of shearing processes appears untenable; unfortunately, no adequate alternative can be advanced other than the statement that the mechanism of diffusionless transformations is certainly much more complicated than that proposed by Kurdjumow and Sachs.

The orientation habit of the platelike austempering structure varies with temperature, and in no case is it the same as that of martensite. The orientation habit of martensite, on the other hand, is constant between 0.9 and 1.4 per cent carbon and between 1.5 and 1.8 per cent carbon; for a given steel there is no variation with temperature of formation or with the speed of cooling through the martensite range. Furthermore, in steels of near-eutectoid composition the austempering structures are consistently platelike, whereas martensite crystals are lathlike. There is, then, reason to differentiate between martensite and austempering structures formed above the martensite range,\* from the point of view of kinetics,<sup>11</sup> of crystallography, and of microstructure.

For 0.92 per cent carbon steel, the change of orientation habit with temperature is along a path that stereographically is a great circle joining an octahedral pole and the center of the cementite pole region;† this great circle is a  $\langle 134 \rangle$  zone of austenite. The fact that this  $\langle 134 \rangle$  direction is also parallel to the fiber axis of cementite certainly cannot be ascribed to coincidence. The inference is that, for this steel, the habits of the austempering products result from a cooperation (or conflict) between the individual growth habits of ferrite and cementite; at high temperatures the ferrite habit predominates, while at low temperatures the cementite habit is more nearly approached. The crystallographic results for 0.92 per cent carbon steel indicate that the austempering structure in eutectoid steel is one product whose properties change gradually and continuously as temperature of formation is varied; the suggestion of Mehl<sup>34</sup> that the austempering product formed "between 400° and 200°" is the same as tempered martensite is not substantiated.

For 1.78 per cent carbon steel, the orientation habits of the austempering products also vary with temperature; it is not possible to state whether

\* The structures that result from constant-temperature decomposition of remaining austenite within the martensite range are characteristically ill formed, and the lower the temperature the more ill formed is this product. Attempts to secure orientation data on the constant-temperature product in specimens of 1.78 per cent carbon steel ( $A_{r''} = 65^\circ$ ) after 8 weeks at 46°C., and of 0.92 per cent carbon steel ( $A_{r''} =$  about 220°) after 17 min. at 200°C. have been unsuccessful to date. It is believed that orientation studies on this constant-temperature product at temperatures only 5° or 10° below  $A_{r''}$  could be carried out successfully.

† For location of cementite poles, see ref. 15.



or not this variation is continuous. Poles of the 200°C. product lie on the [134] zone shown in Fig. 18, but poles of the 100° product do not. The nodular product resulting from the 300°C. decomposition may by some observers be taken to indicate a change in transformation mechanism at this temperature. The structure bears a striking resemblance to primary troostite, and at least on the basis of microstructure these two products would be classified together.

The proposal is advanced that the high-temperature austempering structures are formed as aggregates of ferrite and cementite, and that the main change in the process for lower temperatures is that the role of ferrite is gradually taken over by ferrite containing increasing amounts of carbon in solution. The orientation habit of the platelike shape is controlled by the cooperation or conflict between two lattices that precipitate simultaneously, each tending to grow according to its individual habit. At high temperatures the growth characteristics of ferrite predominate; with decreasing temperature, cementite becomes increasingly important. Once a few molecules of cementite have precipitated at low temperatures, martensite can form isothermally because of carbon depletion in these regions. Points in support of this picture may be listed as follows:

1. The continuous variation in orientation habit of the austempering products with temperature (for steels of near-eutectoid composition). If a single lattice (supersaturated ferrite) were being precipitated at all temperatures, one might reasonably expect the plane of precipitation to remain constant.

2. The fact that some, possibly all, austempering structures form by processes that involve growth.

3. The fact that the austempering shapes for 200°C. and higher in 1.78 per cent carbon steel have a distinct granular or imperfect lamellar structure; martensite tempered for much longer times at these temperatures does not acquire this fine structure.

4. The demonstrated formation of martensite of subnormal axial ratio pseudomorphic to cementite under proper cooling conditions. It is believed that the same precipitation sequence obtains when a specimen is austempered near the martensite range; however, the orientation habit of these visible particles will be controlled by martensite and cementite, and not by cementite alone, as when the martensite is truly pseudomorphic.

Mehl<sup>34</sup> has proposed that the type of reaction changes near 550°C., and that the nucleation processes above and below this temperature are different. The fact that the 450°C. product in 0.92 per cent carbon steel is octahedral might be regarded as confirmation of Mehl's prediction that the "upper bainite" transformation is nucleated by ferrite. This prediction was based upon the extrapolation of a pearlite-spacing vs.



temperature curve, which would give a spacing less than atomic at 560°C., and thus near this temperature a ferrite nucleus would form more readily than would the larger cementite nucleus. However, if this intimate association between nucleation process and habit is accepted, it becomes difficult to account for the demonstrated continuous change of orientation habit with temperature.

Gensamer and co-workers<sup>35</sup> previously suggested that austempering structures might really be lamellar aggregates instead of single-phase particles. This conclusion was motivated by the straight-line relationship they found between physical properties and decomposition temperature for the isothermal products formed in the temperature range between 700° and 350°C. Their evaluated curve for interlamellar spacing vs. temperature is considerably different from the one upon which Mehl based his prediction; instead of a spacing less than atomic near 560°C., a spacing of several hundred Ångströms is indicated at this temperature.

#### SUMMARY

The shapes and orientation habits of the following products of austenite decomposition have been described: (1) martensite in plain carbon and nickel steels, (2) structures resulting from the quenching of 1.78 per cent carbon austenite at rates below the critical cooling velocity, and (3) structures resulting from the austempering treatment in 0.92 and 1.78 per cent carbon steel at various temperatures. The following conclusions have been drawn:

1. In none of the alloys studied does a martensite plate form on a low-index plane of austenite; in 0.35 per cent carbon steel, the martensite crystals are needle-shaped and these crystals form in a platelike array delineating the octahedral planes of austenite. The orientation habit of iron-carbon martensite changes abruptly at a carbon content of about 1.4 per cent. For carbon contents above 1.4 per cent, the habit may be described  $\pm 1^\circ$  as  $\{4\ 10\ 18\}_\gamma$ ; and for lower carbon contents the martensite plates are approximately parallel to  $\{4\ 4\ 10\}_\gamma$ . In steel of near-eutectoid composition, the martensite crystals are lath-shaped and the long dimension of the lath is parallel to  $\langle 110 \rangle_\gamma$ . Carbon (or iron-carbide) plays no role in the formation of the martensite midrib.

2. The subnormal axial ratios for martensite reported by previous investigators are readily explained without assuming a direct dependence of axial ratio upon cooling velocity.

3. The long straight direction contained in cementite plates formed at  $A_r'$  is approximately parallel to  $\langle 134 \rangle$  of austenite.

4. The orientation habit of the platelike products of austempering varies with temperature, and in no case studied is it the same as that of martensite.

5. The structure that results from austempering is distinctly nodular for 1.78 per cent carbon steel at 300°C. (and for 1.4 per cent carbon steel at 350°C.).

It is suggested that austempering products are formed as aggregates, not as single-phase particles.

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## DISCUSSION

(R. S. Archer presiding)

M. H. PAKKALA,\* Kearny, N. J.—Dr. Greninger and Dr. Troiano are to be congratulated on an admirable piece of research work. I can well imagine that it required the polishing of hundreds of surfaces on a single sample in order to obtain the data they here present. They have adequately, it seems, demonstrated that the orientation habits of the martensite plates depend upon the carbon content. However, are the authors convinced that the temperature at which the martensite forms does not also affect the orientation habits, since this temperature varies with carbon content?

C. H. DESCH, London, England.—This work has shown that the structure of martensite, at least in high-carbon steels, cannot be represented as a Widmanstätten structure on a small scale and that the planes on which precipitation occurs may be complex, as in other instances it seems likely that the most closely packed lines in the lattice play a more important part than the closely packed planes.

I am reported in the paper as having suggested that the midrib was a sheet of cementite, perhaps one molecule thick. This is a misunderstanding. My remark did not refer to the midrib but to the fine lines crossing it, which are shown in the high-

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\* Research Laboratory, U. S. Steel Corporation.

power photographs of Lucas. Sometimes these run directly across the midrib and in other places they occupy positions which very strongly suggest twinning. I am by no means sure that in such specimens they are not really twins.

The experiments of Wiester, and especially the kinematographic film which he prepared, of which there is a copy in this country, show very clearly that each martensite crystal formed during isothermal transformation makes its appearance suddenly and is complete from the beginning. The appearance reminds one strongly of the formation of twins on deforming zinc or of Neumann lines in iron. This formation, being so sudden and showing itself on the free surface of the metal by the throwing up of the new crystal into relief, must occur by a process of shear whether simple or complex. In that case there must be a close relation between the principal planes of the martensite crystal and of the austenite from which it was formed. When the structure of cementite has been determined with more certainty and its relation to martensite fixed, it should be possible to represent the mechanism of the change more definitely.

J. R. VILELLA,\* Kearny, N. J.—The part of this paper dealing with the nodular structure occurring in steels of more than 1.40 per cent carbon when transformed isothermally at temperatures in the vicinity of 300°C. (570°F.) is of particular interest. Even though this structure occurs only in steels that, because of their slight industrial significance, have not been examined as closely as those of lower carbon content, it is, nevertheless, of considerable metallographic interest to observe what appears to be another variation of the bainite group of structures. The fact that this nodular variation was observed the first time that the isothermal transformation of these high-carbon steels was studied attests once more to the fruitfulness of this method of investigation.

Because the photomicrographs of this structure presented by the authors are at a magnification too low to reveal its extreme fineness of detail, it was deemed that a series of high-power photomicrographs showing how the structure varies with the transformation temperature would constitute a supplement of some value to this interesting paper.

The accompanying photomicrographs (Figs. 23 to 29) were obtained from specimens of 1.60 per cent carbon steel which were heated 10 min. at 1090°C. (2000°F.) and partly transformed isothermally at the temperatures indicated. All but Fig. 1 were made with an oil-immersion objective of numerical aperture 1.4 at a magnification of 2000 diameters. The etchant was 4 per cent Pieral.

In Figs. 23 and 24, at 300°C. (570°F.) the first structure to appear at the austenite grain boundaries is not nodular but columnar; nodules appear only in the interior of the grains and exhibit a decided tendency to be hexagonal rather than circular. The advancing fronts of transformation appear to be more rectilinear than can be associated with the growth of ordinary nodules. It may be seen in Fig. 24 that the fineness of the carbide and ferrite distribution within the structure is beyond the resolving power of the objective used.

At 325°C. (615°F.) the structure is more nearly nodular, both at the grain boundaries and in the interior of the grains, although a slight tendency to be columnar was observed occasionally at the grain boundaries. While the structure is too fine to be resolved, it is not quite as fine as that obtained at 300°C. (570°F.). (Fig. 25.)

The product of transformation at 350°C. (660°F.) shown in Fig. 26 appears as though made up of two different structures, a lighter-etching one similar to the feathery bainite obtained in eutectoid steel transformed in the neighborhood of 480°C. (900°F.) and a darker-etching one of finer texture occurring as wedge-shaped blocks. This impression of two distinct structures is probably more apparent than real and

\* Research Laboratory, U. S. Steel Corporation.



can result from differences in orientation of the structure with respect to the plane of polishing. Note that the isolated nodule shown in this photomicrograph contains a nonmetallic inclusion at the center. This is a frequent occurrence in the nodules produced at all temperatures, and may account for the circular shape of the structure

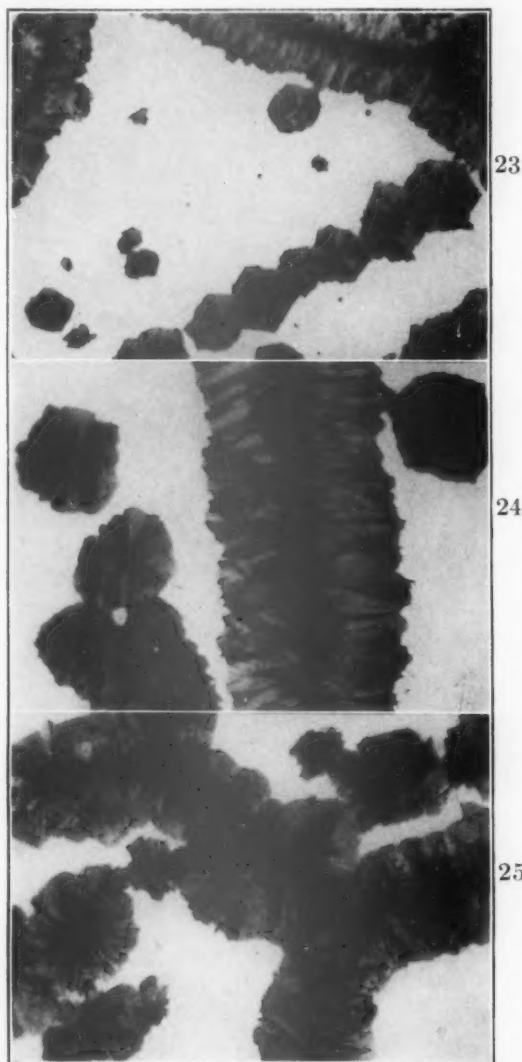


FIG. 23.—TRANSFORMED AT 300°C. (570°F.).  $\times 1000$ .  
FIG. 24.—TRANSFORMED AT 300°C. (570°F.).  $\times 2000$ .  
FIG. 25.—TRANSFORMED AT 325°C. (615°F.).  $\times 2000$ .  
Original magnifications given; reduced  $\frac{1}{2}$  in reproduction.

within the grains. Seven nodules out of one hundred examined exhibited center inclusions; considering the relative size of the nodule and inclusion, such a proportion of exposed inclusions in the center of the nodules (sectioned through the center during polishing) can be expected only when a much larger number of nodules contain center inclusions. It seems highly probable, therefore, that the nonmetallic inclusions serve as nuclei from which the transformation spreads radially in all directions.

The 375°C. (705°F.) structure (Fig. 27) differs from those obtained at lower temperatures in two respects; it is of somewhat coarser texture—that is, better



resolved by the same objective—and its shape is becoming more nearly like that of the bainites formed in lower carbon steels. The 400° and 450°C. (750° and 840°F.) structures (Figs. 28 and 29, respectively) are perhaps of slightly coarser texture and definitely more acicular in shape than the 375°C. (705°F.) product. These are indistinguishable from the ordinary bainites of lower carbon steels. However, a tendency still persists to form irregular clusters of needles in the center of which can be seen occasionally a nonmetallic inclusion (Fig. 28).

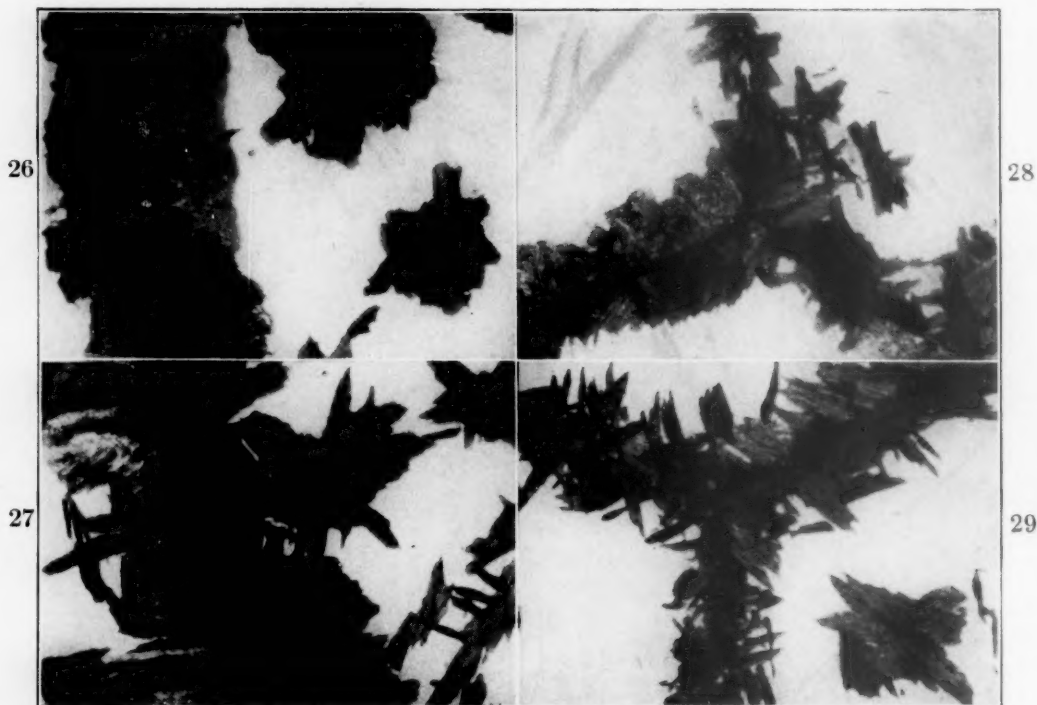


FIG. 26.—TRANSFORMED AT 350°C. (660°F.).

FIG. 27.—TRANSFORMED AT 375°C. (705°F.).

FIG. 28.—TRANSFORMED AT 400°C. (750°F.).

FIG. 29.—TRANSFORMED AT 450°C. (840°F.).

Original magnification 2000  $\times$ ; reduced  $\frac{1}{2}$  in reproduction.

It may be said, by way of summary, that the structures produced by isothermal transformation in steels of more than 1.40 per cent carbon at temperature between 300° and 450°C. (570° and 840°F.) form a continuous series of structures similar to the bainites of lower carbon steels but exhibiting a strong tendency to form nodular or radial structures rather than the acicular, martensitlike structure of the lower carbon bainites. When the austenite grain boundaries act as nuclei for the beginning of the transformation, the structure tends to be columnar, but when a nonmetallic inclusion in the interior of a grain serves as the starting point, the structure becomes radial or nodular.

R. F. MEHL,\* Pittsburgh, Pa.—There can be no question but that this very precise work must supersede previous work on composition planes and directions in the geometric figures which appear in the formation of martensite. These are evidently more complicated than previously thought. G. V. Smith, at Carnegie Institute of Technology, has found also that the composition plane in bainite-formed isothermally at 450°C. is the {111} plane, as shown by these authors.

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It probably is worth stating, however, that trace directions and composition planes alone are but part of the problem of the crystallographic mechanism of solid-solid reactions. It has been observed frequently that composition planes may be complicated or perhaps irrational when the orientation relationships are relatively simple; it has also been observed in the copper-silver system that the composition planes may differ but the orientation relationships be identical; it does not follow, for example, that the orientation relationships should vary with the temperature of decomposition of austenite even though the composition planes do. It may be stated that a determination of the composition planes and a study of the outward form of the decomposition product furnishes information on the crystal habit only. This is true, but the significance of composition planes is somewhat greater than this, for such information must be considered in deriving possible shearing mechanisms by which the old lattice may transform to the new.

Thus we need information on both the composition planes and the orientation relationships before a full description of the mechanism may be written. Either alone may lead to conclusions concerning the mechanisms which are deceptive.

G. SACHS,\* Cleveland, Ohio.—I am somewhat confused by the variety of the observed structures. I agree with the authors that no definite conclusions can be drawn at the present time from their microscopical observations regarding the crystallographic mechanism of the austenite decomposition. Therefore, I do not quite understand how the authors came to the conclusions that their results are inconsistent with the much discussed shear mechanism of the martensite transformation.<sup>17,19,20</sup> While there are two varieties known of such a transformation mechanism, the crystallographic relations in either case have been repeatedly confirmed within an accuracy of a couple of degrees of even better than a degree. For instance, if tetragonal martensite exists, the expected deviation by a few degrees of the crystal axes from those of the cubic ferrite has been experimentally confirmed.

On the other hand, the angular relations reported by the authors show considerable scattering and I wonder whether this is caused by the experimental difficulties or by the fundamental irregularities of the boundaries of the martensite plates. I agree with the authors that these "crystals" probably originated by a process of nuclei formation and crystal growth. I am, however, somewhat reluctant to accept a conclusion from the external boundaries on the internal structure, which appears at present both of a simpler nature and better confirmed. I would assume, on the contrary, that very different basic principles underlie these two processes. While crystal nuclei may be formed by a definite crystallographic process similar to mechanical twinning, crystal growth is determined by the statistical laws of thermal movement or diffusion.

A. B. GRENINGER AND A. R. TROIANO (authors' reply).—In answer to Mr. Pakkala's question: It appears quite safe to state that, for a constant carbon content, the orientation habit of martensite is independent of formation temperature. It is, of course, not possible to consider temperature and carbon content as independent variables, inasmuch as it is impossible to change carbon content without changing the temperature range within which martensite will form on cooling. However, it should be emphasized that the orientation habit of martensite does not really *vary* with carbon content. The composition plane remains constant for steels between 0.9 and 1.4 per cent carbon, and is also constant for steels between 1.5 and 1.8 per cent carbon.

We regret that we have misinterpreted Dr. Desch's remarks concerning the cross lines in martensite crystals. We have, incidentally, devoted considerable time to a study of these cross lines; this study is being continued. We assume that Dr. Desch did not intend to state that the martensite crystals studied cinematographically by

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Wiester were formed during *isothermal* transformation. In the study referred to, Wiester quenched a specimen of 1.7 per cent carbon steel into a liquid metal bath held at 100°C., polished the specimen while it was held at this temperature, then photographed the process of martensite formation (as a surface-relief effect) during subsequent cooling to room temperature. The martensite formation photographed by Wiester took place during cooling and not during isothermal transformation of austenite. Wiester's technique has been applied to studies of martensite transformations of nonferrous alloy systems.<sup>30,36,37</sup> In a recent publication<sup>11</sup> we have presented experimental proof for the statement that at least in eutectoid and hypereutectoid steels martensite forms from austenite only during cooling through the proper temperature range.

We welcome Mr. Vilella's photomicrographic supplement to our paper. An interesting point is that the temperature of the appearance of this nodular product may be correlated, to a certain extent, with a change in reaction rates, as follows: At temperatures above about 300°C., the decomposition rate of 1.8 per cent carbon austenite is more rapid than that of austenite having a lower carbon content; whereas, for temperatures below 300°C., the reverse is true.

We are happy to note that Mr. G. V. Smith has also found the composition plane of 450° bainite to be the {111} plane. We assume that these results, quoted by Dr. Mehl, refer to steel of near-eutectoid composition. We have found that the orientation habit of bainite is controlled by carbon as well as temperature. In the 1.78 per cent carbon steel, the platelike isothermal product first appears at a decomposition temperature of about 500°C. The 500°C. (and 450°C.) product in this steel has an orientation habit that is definitely not octahedral, but apparently is very similar to that of the 350°C. product in 0.92 per cent carbon steel.

Dr. Sachs evidently regards the terms "lattice relationships" and "shear mechanism" as inseparable; at least, the impression is conveyed that because the *crystallographic relations* have been confirmed by several investigators, the *postulated shear mechanism* must necessarily be the actual mechanism of martensite formation. We must disagree with Dr. Sachs. There can be no doubt that the austenite-martensite lattice relationships, originally described by Kurdjumow and Sachs for 1.4 per cent carbon steel, are approximately correct—probably not in error by more than two or three degrees. As long as the martensite plates were believed to form parallel to octahedral planes of austenite, the shear mechanism of Kurdjumow and Sachs appeared plausible. Now, however, we know that the martensite plates form parallel to {4 10 18} or {4 4 10}, and that the midrib planes show excellent parallelism. Faced with these new facts, we cannot see any justification at present for a shearing mechanism that postulates a shear initiating on any low-indices plane of austenite. We believe the midrib, and thus the midrib plane, to be an integral part of the real transformation mechanism; and any postulated mechanism that does not account for the irrational orientation habit of the midrib plane is at least inadequate, perhaps entirely wrong. As mentioned in the paper, Phragmén has previously discussed the disparity between our experimental results and the shear mechanism proposed by Kurdjumow and Sachs. We did not elaborate upon these discrepancies primarily because our paper was not directly concerned with lattice relationships. We are at present engaged in a study of lattice relationships for the austenite-martensite transformation, using the technique previously employed by one of us on the martensite reactions in beta copper-aluminum alloys.<sup>31</sup> We have succeeded in obtaining excellent back-reflection Laue patterns from individual crystals of martensite in steel; this method of study is proving to be extremely useful not only in accurate evaluation of lattice relationships, but also in studies of the behavior of martensite during tempering.

<sup>36</sup> I. Obinata and M. Hayashi: On the Nature of the Transformation of Aluminum Bronze, V.—Change in Structure Due to the Transformation. *Jnl. Japan Iron and Steel Inst.* (1937) **23**, 1092–1099. (In Japanese with English synopsis.)

<sup>37</sup> V. Gridnev and G. Kurdjumow: Transformations in Eutectoid Cu-Al Alloys, III.—Reversible Transformation of the  $\beta$ -Solid Solution in the Metastable State. *Tech. Phys. U.S.S.R.* (1938) **4**, 1–16.

## Study of Lattice Distortion in Plastically Deformed Alpha Iron

BY NORMAN P. GOSS,\* MEMBER A.I.M.E.

(New York Meeting, February 1939)

It is generally agreed that cold-working mechanically refines the grains into smaller fragments and with continued working these are oriented with certain crystallographic directions bearing a relation to the direction in which the metal is worked. Some of the energy expended on the metal during plastic deformation appears in the form of heat, but a very small portion remains in the metal as stored energy. The entropy, specific heat capacity, temperature at which recrystallization will just begin, density, ductility, elasticity, tensile strength, and resistance to corrosion are affected. These properties have been studied extensively and some of the changes in the physical properties due to cold-working were attributed to lattice distortion.<sup>1-8</sup>

The broadening of the  $K_\alpha$  lines on the X-ray diffraction diagrams of plastically deformed metals is believed to indicate lattice distortion, and consequently the existence of internal stresses. The evidence supporting this theory rests solely upon the observed experimental fact that the diffraction lines are broadened and the  $K_\alpha$  doublets are completely diffused.

Elam<sup>9</sup> has reviewed the matter of lattice distortion in relationship to the hardening of metals by plastic deformation. The X-ray diagrams of plastically deformed metals differ in general from annealed metals. The hardening of a metal was believed due to lattice distortion.<sup>9</sup> The resolution of the doublet is lost when a metal is cold-worked and the Laue spots are elongated. At one time this elongation was thought to indicate the elastic bending of the crystal planes. However, more careful work showed that the asterism was due to new orientations developed within the fragmented grains during plastic deformation. Some theories attributed the hardening to fragmentation of the grains into smaller units.

Jeffries and Archer,<sup>11</sup> after carefully considering the problem of work-hardening from many angles, came to the conclusion that cold-working mechanically refines the grains into smaller crystal fragments, some of which at least differ in orientation from the parent grain. The increase in

Manuscript received at the office of the Institute Nov. 29, 1938; revised March 18, 1940. Issued as T.P. 1218 in METALS TECHNOLOGY, August 1940.

\* Physicist, Cold Metal Process Co., Youngstown, Ohio.

<sup>1</sup> References are at the end of the paper.



hardness is attributed to such fragmentation and does not require the assumption that the crystal lattice is distorted.

Maier<sup>10</sup> studied, experimentally, the changes in the density of cold-worked copper and iron and concluded that this was due to lattice distortion, because of the great mass of X-ray data in favor of it. Nevertheless he pointed out that from a thermodynamic point of view a decrease in specific heat capacity is required when the space lattice is expanded; but it is a well established experimental fact that the specific heat capacity is increased slightly.

The lattice distortion theory therefore fails to explain certain energy changes that accompany plastic deformation as pointed out by Maier. Further X-ray diffraction studies are warranted with improved technique, in order to gain a clearer idea of the extent of lattice distortion.

#### MODIFIED PRECISION X-RAY SURFACE DIFFRACTION METHOD

To obtain the sharpest possible lines and  $K_\alpha$  doublet resolution in plastically deformed metals the following factors of technique should be considered.

1. As the particle size of a metal becomes smaller and smaller it becomes more and more difficult to resolve the  $K_\alpha$  doublets and obtain sharp diffraction lines. A divergent X-ray beam cannot be used in the study of small particle size. However, when a parallel beam of X-rays is used sharper lines and resolved  $K_\alpha$  doublets can be obtained when small particle sizes are X-rayed. The smaller the particle size, the more nearly parallel the X-ray beam must be. An absolutely parallel beam of X-rays can never be realized, but it can be made less and less divergent by the use of a long enough slit system.

2. The carefully defined X-ray beam must strike the specimen at the proper angle of incidence. The smaller the particle size, the greater the angle of incidence must be in order to obtain sharp doublet resolution.

3. The cassette must be of sturdy construction accurately made so that exact duplication of results can be obtained, permitting comparison of line position and line resolution.

The cassette shown in Fig. 1 was designed to incorporate these requirements. In one view the specimen holder is removed, to show the construction and method of mounting the specimen. The holder was machined in such a way that the surface of the specimen contains the axis of the cassette. The specimen is firmly held in place by means of two Allen setscrews. The bearing into which the holder fits and the slot for the Bakelite cylinder that supports the film were machined on a precision milling machine simultaneously, thus assuring accurate alignment of the specimen and film. The protractor, graduated in degrees, is shown in the other view of Fig. 1. It can be read to 30 sec. of arc, thus permitting accurate setting of the specimen at any angle to the X-ray beam. Each



cassette is supplied with several interchangeable slit systems. The one shown beside the cassette in Fig. 1 has 0.010 by 0.375 in. slits placed 3.5 in. apart and very accurately aligned. The largest one used has a 0.020 by 0.375-in. aperture placed in each end of the collimator.

Experiment proved that very little is gained by using slits smaller than 0.010 in. In fact, the 0.015-in. slit system is nearly as good; the time of exposure is reduced, and the X-ray beam is almost parallel, and only a slight loss in line sharpness is experienced. The same reasoning holds true for the 0.020-in. slit system. Sharp lines can be obtained but a larger angle of incidence must be used.

The slit system is mounted in the cassette so that the path of the X-ray beam bisects the axis of the cassette parallel to the surface of the specimen.

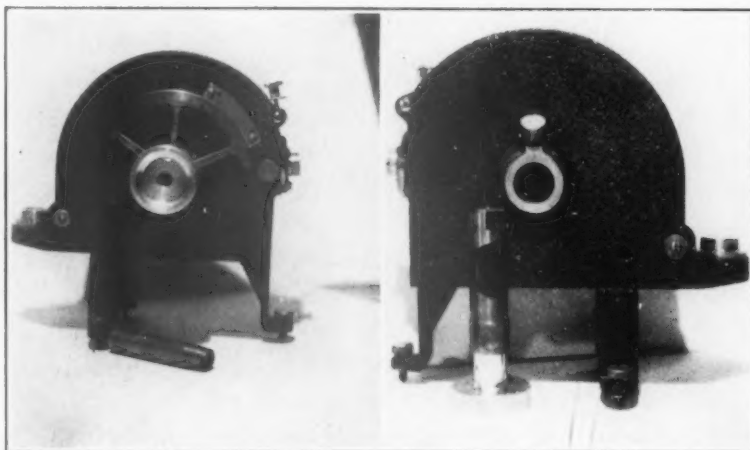


FIG. 1.—TWO VIEWS OF SURFACE-DIFFRACTION CASSETTE.

Three interchangeable slit systems are provided, with apertures of 0.010, 0.015 and 0.020 in. spaced 3.5 in. apart. When spaced this distance apart a substantially parallel beam of X-rays is obtained. Specimen is held firmly in the holder shown. It is so constructed that surface of specimen contains axis of cassette. X-ray beam bisects axis of cassette. Radius of cassette is 3.5 inches.

The radius of the cassette is about 3.5 in. and the X-ray film is placed on the radius of curvature and held in place by a bronze band clamped at one end by a thumbscrew.

#### PREPARATION OF SPECIMENS AND EXPERIMENTAL DETAILS

Two types of low-carbon hot-rolled strip were used, one a rimming steel (0.15 per cent C) and the other a 0.02 per cent C ingot iron. The rimmed steel was rolled on a continuous hot mill and finished at 1500° to 1600°F. Under the microscope the grains were observed to be small and equiaxed, but the central portion of the strip was banded, which usually is associated with a high degree of manganese sulphide segregation. The ingot iron was finished at about 1400°F. The grains were found to be elongated when examined under the microscope, which is attributed to the low finishing temperature.

The hot-rolled strip was pickled to remove the scale and then cold-rolled. (The hot-rolled strip was not annealed before cold-rolling.) The cold-rolling was performed on a laboratory two-high mill. By using small samples and light reductions per pass it was assured that neither the rolls nor the strip suffered appreciable increase in temperature during the cold-rolling process. However, it must be said that no matter how small the reduction may be some heat will be generated because of internal friction; however, this heat can be kept from becoming excessive. Experience has shown that the metal hardens in approximately the same way over a considerable range of rolling temperature.

The rimmed steel was cold-rolled with the following reductions in thickness:

- 0.102 to 0.075 in., 26.5 per cent reduction in thickness
- 0.102 to 0.015 in., 85.0 per cent reduction in thickness
- 0.102 to 0.005 in., 95.0 per cent reduction in thickness

The ingot iron was cold-rolled from 0.079 to 0.019 in., which is a reduction of 76 per cent in thickness. Another sample of ingot iron was cold-rolled from 0.079 to 0.048 in. and heat-treated at 1650°F. for 24 hr. in a reducing atmosphere. The annealed strip was rolled from 0.048 to 0.017 in. on a laboratory cold mill. The cold-reduced strip was examined by the surface diffraction method before being heat-treated and again after it had been heat-treated at 1700°F., without removing the X-ray film from the cassette. The X-ray diagrams of the cold-worked and annealed ingot iron were therefore superimposed.

Another specimen of large-grained ingot iron in which the grains varied from  $\frac{1}{8}$  to  $\frac{1}{4}$  in. in diameter was cold-rolled from 0.048 to 0.011 in. A 0.90 per cent C hot-rolled strip steel 0.082 in. thick was cold-rolled directly to 0.025 in. without any intermediate heat-treatments, a total reduction of 69.5 per cent.

After cold-rolling the specimens were prepared for X-ray examination by being cut to fit the space provided in the specimen holder of the reflection cassette. The surface from which the X-ray beam is diffracted must be flat and the axis of the cassette must lie in the surface of the specimen. Each specimen was tested for flatness and carefully etched in a 10 per cent Nital solution before it was mounted in the cassette holder.

The X-ray diffraction diagrams were made with the surface-diffraction cassette shown in Fig. 1. The only variables were the angle of incidence and the size of aperture used in the slit systems. Three sizes of slit systems were used—0.010, 0.015, and 0.020 in. The angle of incidence used was the one at which the  $K_{\alpha}$  doublets could be sharply resolved, and it varied from 17° to 40° or more, depending entirely upon the fragment size of the plastically deformed grains.

The source of the X-rays was a General Electric tube having a molybdenum target. It was operated at 35,000 volts and 12 ma-hr.

Some of the X-ray diagrams were made with monochromatic radiation and others with polychromatic along with the monochromatic radiation. The  $K_{\alpha}$  doublets could be resolved by using either form of radiation.

#### SURFACE DIFFRACTION DIAGRAM OF PLASTICALLY DEFORMED ALPHA IRON

Fig. 2 is an X-ray diffraction diagram of a low-carbon rimmed steel that was cold-rolled from 0.102 to 0.075 in. The slits were 0.015 in. and the angles of incidence  $14^{\circ}$  and  $25^{\circ}$ , respectively. The  $K_{\alpha}$  doublets were found to be resolved in both of these X-ray diagrams, but much more sharply resolved in the one in which the angle of incidence was  $25^{\circ}$ . A great deal of detail that appears on the negative is lost in printing, and for this reason the prints never show the true sharpness of the line structure. These X-ray diagrams do show that line sharpness depends upon the angle of incidence and the smaller the particle size, the greater the angle of incidence must be. These X-ray diagrams also show that it is possible to resolve the  $K_{\alpha}$  doublets when a beam of X-rays is reflected from the surface of a plastically deformed metal, provided it is substantially parallel. Resolution of the  $K_{\alpha}$  doublets cannot be expected when a divergent beam of X-rays is used.<sup>12</sup>

The line positions of this X-ray diagram were compared with the X-ray diagram of this same specimen after annealing at  $1500^{\circ}\text{F}$ . and slow cooling in the furnace. The two X-ray diagrams are compared in Fig. 3. The line positions were found to be identical and the  $K_{\alpha}$  doublets resolved. Photometer records showed the line widths of these two films to be the same. Much detail is lost in the reproduction of these films but the original negatives clearly show that the intensity of the higher order lines of the plastically deformed strip are diminished. This is attributed to the smaller particle size of the cold-worked strip.

The X-ray diffraction diagram of the ingot-iron specimen given a reduction in thickness of 76 per cent is shown in Fig. 4. The X-ray beam made an angle of  $25^{\circ}$  with the surface of the specimen. The  $K_{\alpha}$  doublets are resolved and the lines are sharply defined, in spite of this drastic deformation. The intense first order (211) line is resolved on the original X-ray film even though the separation of the doublet is less than 0.005 in. The well defined (321) line is resolved and can easily be observed even in the reproduction.

Another X-ray diffraction diagram was made using the 0.010-in. slit system and the same angle of incidence, also shown in Fig. 4. The lines are sharper and the  $K_{\alpha}$  doublets resolved more distinctly, but the differences do not show clearly in the reproduction. However, it establishes the experimental observation that sharpness of lines and resolution of the  $K_{\alpha}$  doublet depend to some extent upon the aperture size, especially when the particle size becomes small enough.

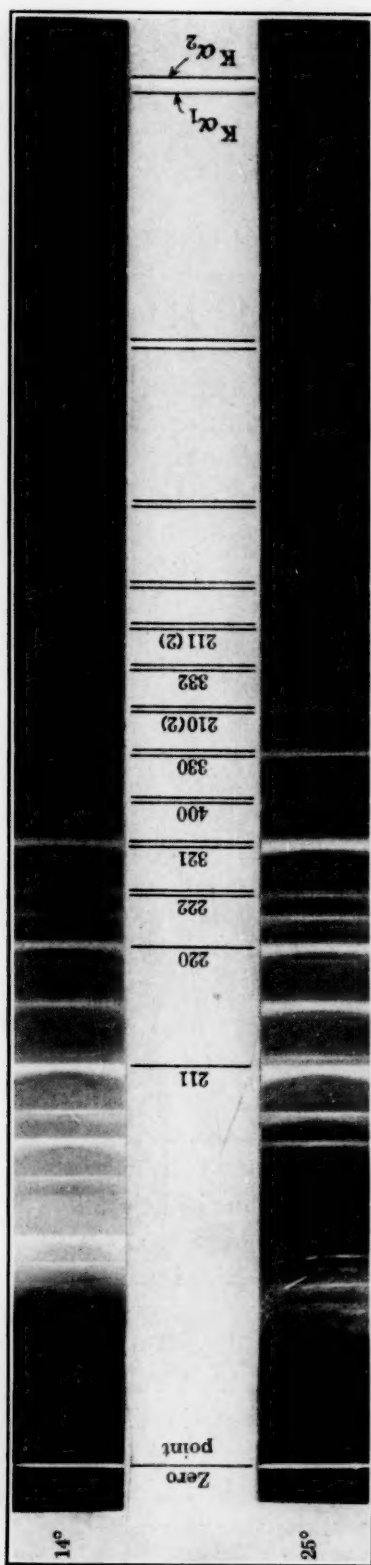


FIG. 2.—LOW-CARBON STRIP STEEL, COLD-ROLLED FROM 0.102 TO 0.075 INCH ON TWO-HIGH LABORATORY MILL. SHOWN AS COLD-ROLLED. These diffraction diagrams were made by using two angles of incidence—one 14° and the other 25°.  $K\alpha$  doublets are merged except for highest order lines and indices when angle of incidence is only 14°. Changing angle of incidence to 25° sharply resolves  $K\alpha$  doublets. To further improve sharpness of  $K\alpha$  doublet, it is only necessary to use either a smaller aperture or a longer slit system. Molybdenum radiation; no filter used; exposure time, 570 ma-hr.; 0.015-in. slit system.

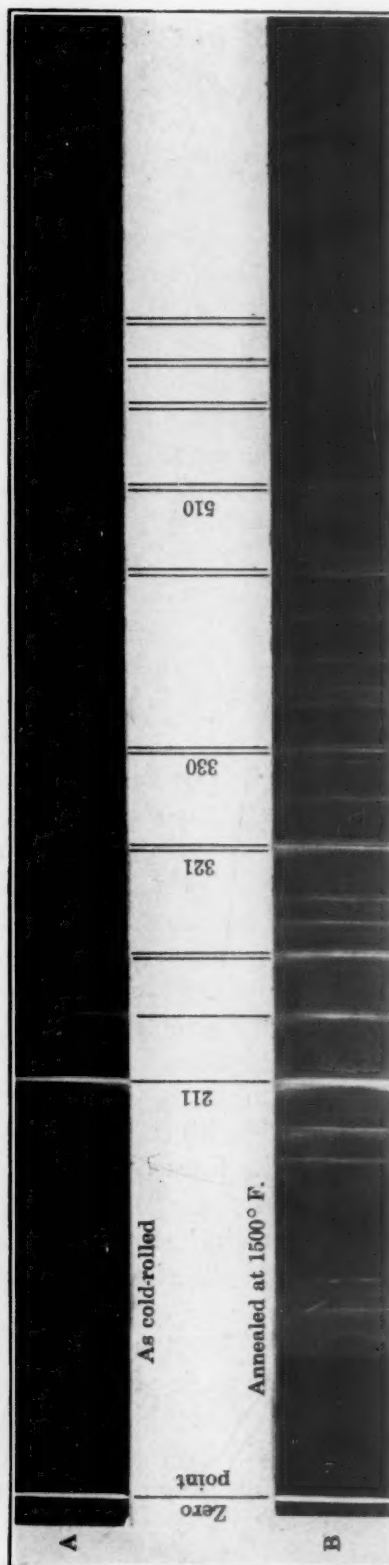


FIG. 3.—LOW-CARBON STRIP STEEL, COLD-ROLLED FROM 0.102 TO 0.075 INCH ON TWO-HIGH MILL, ANNEALED AT 1500° F. FOR 30 MINUTES AND SLOWLY COOLED IN FURNACE.

Angle of incidence, 25°, same as used in one diagram of Fig. 2. Line positions were compared by placing X-ray film of cold-rolled specimen upon X-ray diagram of same specimen after heat-treatment and matching zero lines. When this is done all of the  $K\alpha$  lines coincide perfectly. However, the  $K\alpha$  doublets are sharply resolved. Much detail is lost in reproduction of negatives, especially resolved  $K\alpha$  doublets of lines of higher order and indices. The intensity of higher order lines is reduced in the cold-worked metal, owing to decrease in particle size.  $\mu_{33}$  Molybdenum radiation; white and monochromatic radiation; 0.020-in. slit system; exposure time, 570 ma-hr. for A, 576 ma-hr. for B.



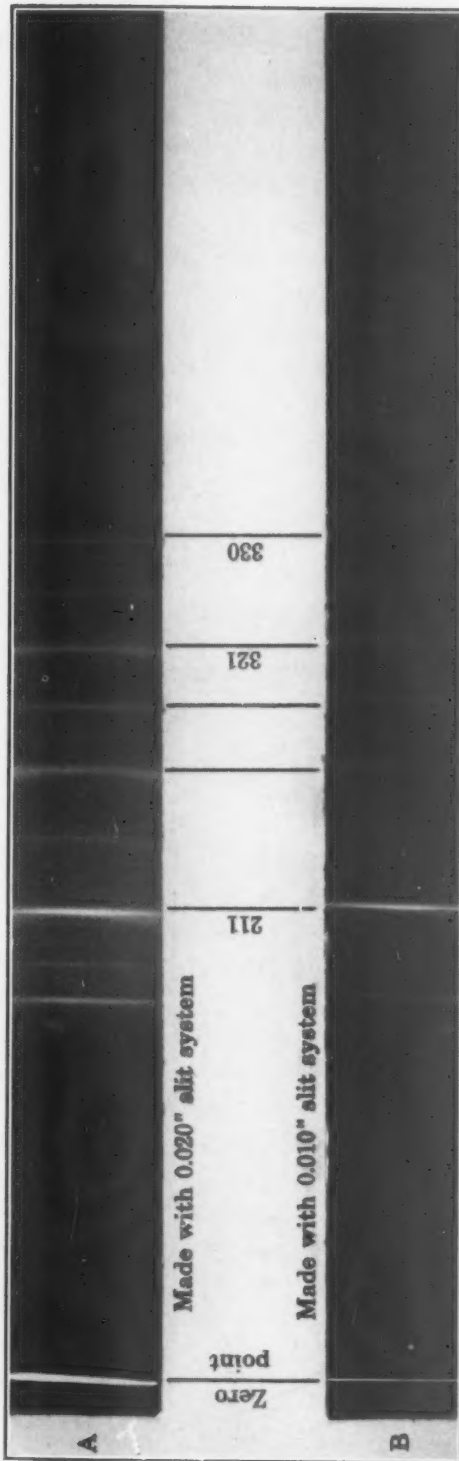


FIG. 4.—INGOT IRON COLD-ROLLED FROM 0.079 TO 0.019 INCH ON TWO-HIGH MILL. Negatives show resolution of  $K_{\alpha}$  doublets but reproductions are not as clear.  $K_{\alpha}$  doublets of (321) and (320) lines can be observed. Molybdenum radiation; zirconia filter; 0.020 and 0.010-in. slit systems; 1195 ma-hr. for A, 1147 ma-hr. for B; angle of incidence,  $25^{\circ}$ .

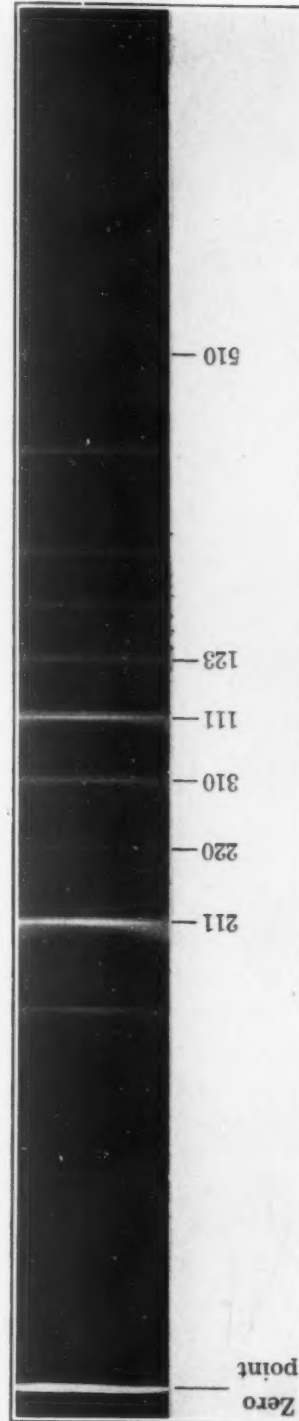


FIG. 5.—LOW-CARBON STRIP STEEL COLD-ROLLED FROM 0.102 TO 0.015 INCH ON TWO-HIGH MILL.  $K_{\alpha}$  doublets appear to be more clearly resolved in a strip given area reduction 85 per cent then one given only a reduction of 76.5 per cent. See Fig. 4. Molybdenum radiation; zirconia filter; 0.020-in. slit system; 570 ma-hr.; angle of incidence,  $25^{\circ}$ .



The effect of aperture size and line sharpness was investigated thoroughly. A drastically cold-rolled specimen was arbitrarily set at  $10^\circ$  to the X-ray beam and surface diffraction diagrams were made, using slit systems having apertures ranging from 0.010 to 0.040 in. and spaced 3.5 in. apart. The results were as expected, the lines in the X-ray diagram made with the 0.010-in. slit system were extremely sharp and the doublets of the higher order lines resolved, while those made with the 0.040-in. slit system exhibited broadened lines and the  $K_\alpha$  doublets were more or less merged except for the lines of very high order or indices. It was interesting to find that the  $K_\alpha$  lines of the doublet were broadened and poorly defined when the 0.040-in. slit system was used. This experiment at least proves that the matter of X-ray technique is important although often considered of secondary importance in metallurgical research. Its importance is stressed in some textbooks.<sup>12</sup>

The intensity of higher order  $K_\alpha$  lines is strongly affected by the fragment size of the plastically deformed grains. The smaller the fragments, the less the intensity of these lines. The problem of particle size and line intensity is beyond the scope of this paper. However, if the experimental and theoretical considerations advanced here are found to be correct (after other investigators have had an opportunity to reproduce the experimental method used in this study) the problem of plastic deformation will no longer be associated with lattice distortion but essentially with particle size, provided the grain fragments are not colloidal in magnitude. It is doubtful whether it will be possible to resolve the  $K_\alpha$  doublets when the particle size approaches colloidal magnitude, but by making the beam even more parallel than in this experiment, sharper lines should be obtained.

No evidence of lattice distortion could be observed in the rimmed steel given a reduction of 85 per cent in thickness; the X-ray surface-diffraction diagram of Fig. 5 shows no evidence of lattice distortion. The  $K_\alpha$  doublets are resolved even in the lower order lines, which in itself is remarkable. The (211) line is clearly resolved on the negative even though the separation of the doublet lines is less than 0.005 in., and this could be accomplished with the slit system having the largest apertures (0.020 in.) and using an angle of incidence of  $25^\circ$ . The intensity of the higher order lines was reduced to a greater degree than the X-ray diagram made of the strip given a 26 per cent reduction (Fig. 3). Reduced intensity is due to the smaller fragment size.

In Fig. 6 a surface-diffraction diagram made of a low-carbon strip steel given a reduction of 95 per cent in thickness is presented. The  $K_\alpha$  doublets are clearly resolved and it was rather surprising to find the intense (111) line clearly resolved. The separation can be observed in the reproduction. This can only mean that even the most severe plastic deformation does not distort the space lattice and that the grain frag-

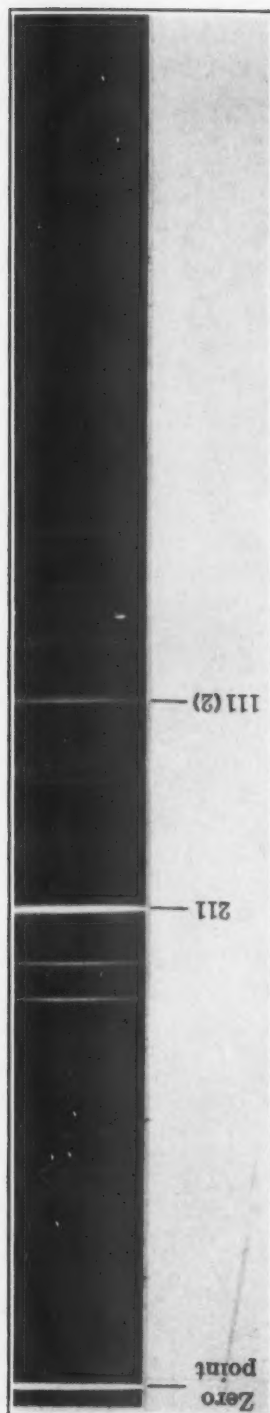


FIG. 6.—LOW-CARBON STRIP STEEL (0.10 PER CENT C) COLD-ROLLED FROM 0.105 TO 0.005 INCH, A REDUCTION IN THICKNESS OF 95 PER CENT.

$K_{\alpha}$  doublet of 111 line (second order) is sharply resolved.

Molybdenum radiation; no filter; 0.020-in. slit system; 570 ma-hr.; angle of incidence,  $25^{\circ}$ .

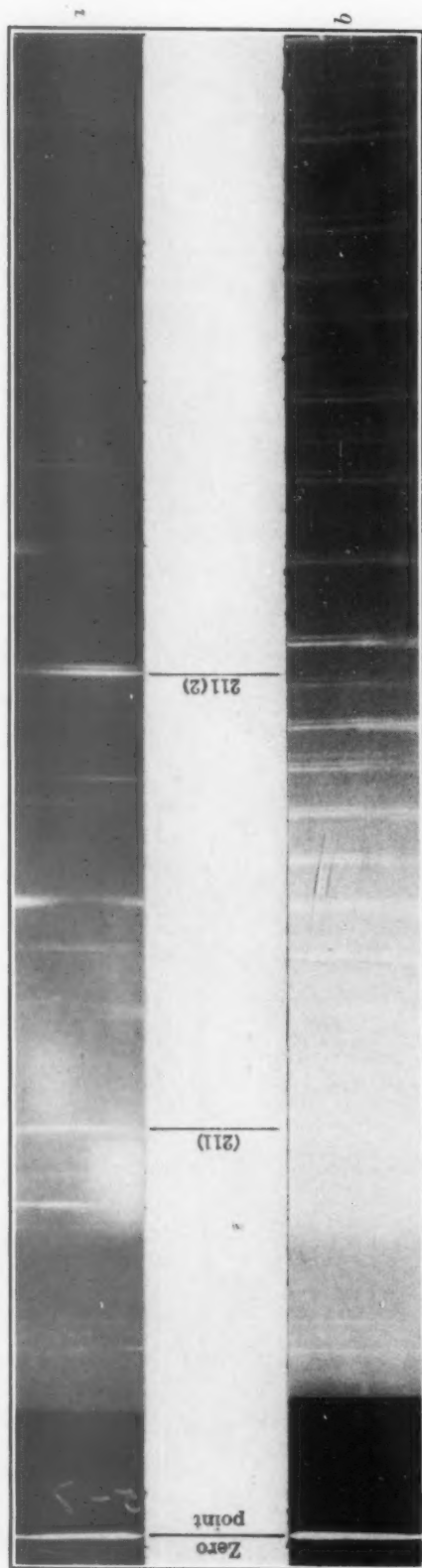


FIG. 7.—LARGE-GRAINED INGOT IRON COLD-ROLLED FROM 0.048 TO 0.017 INCH ON TWO-HIGH MILL.

*a.* Grains in annealed strip were  $\frac{1}{8}$  to  $\frac{1}{4}$ -in. diameter. Note how sharply (211)(2) is resolved.

Molybdenum radiation; zirconia filter; 0.020-in. slit system; angle of incidence,  $25^{\circ}$ ; 1020 ma-hr.

*b.* Cold-rolled specimen was placed in cassette and X-ray film given an exposure of 1725 ma-hr. Specimen was carefully removed, without disturbing film, and heat-treated at  $1700^{\circ}\text{F}$ ., then replaced in cassette. X-ray spectrogram of annealed specimen was superimposed on cold-rolled spectrogram. Exposure for annealed specimen was 1050 ma-hr. Line positions coincide exactly, for the  $K_{\alpha}$  lines remained very sharp. The slightest displacement would have blurred the lines.

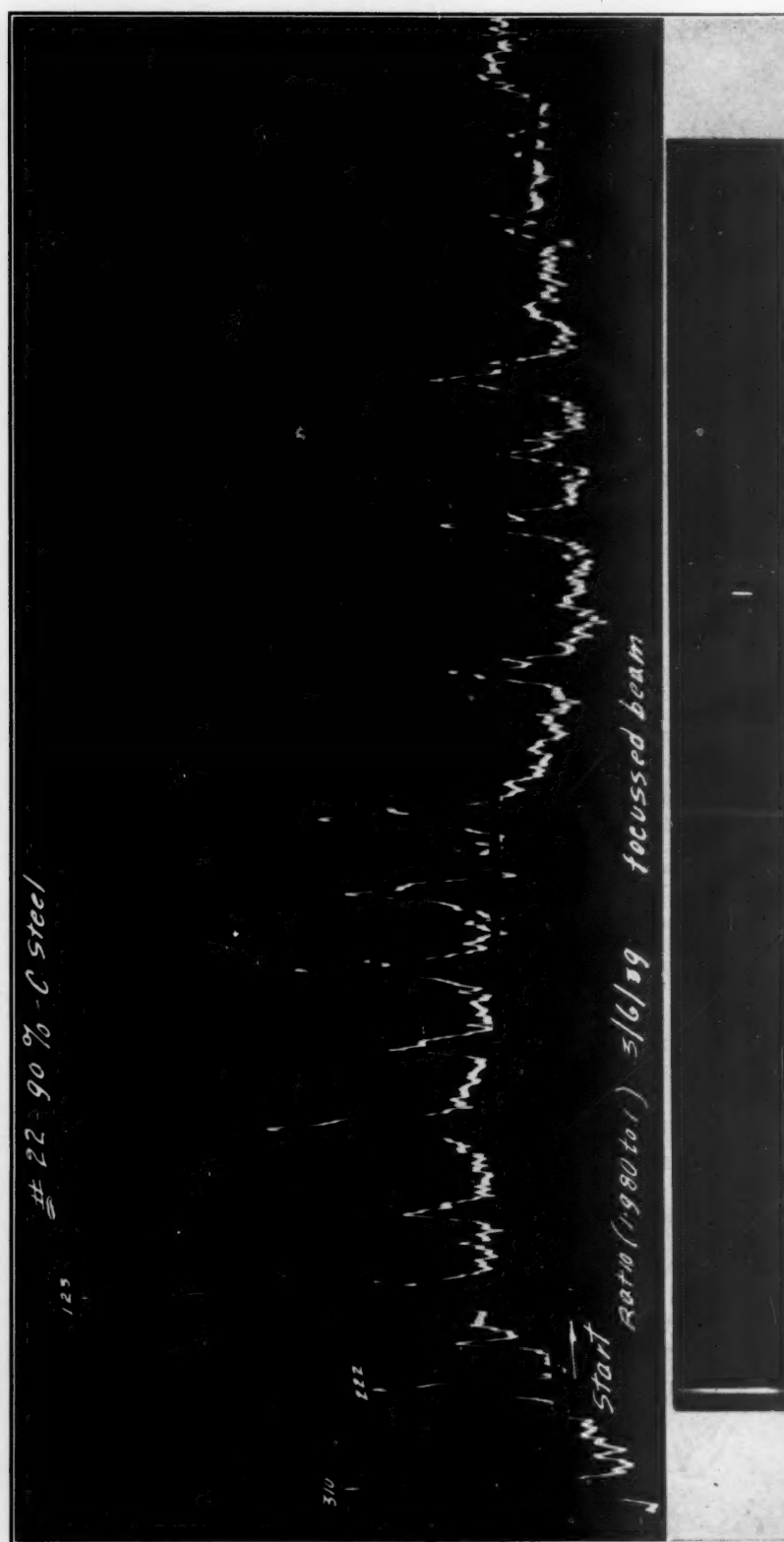


Fig. 8.—0.90 PER CENT CARBON STRIP STEEL COLD-ROLLED FROM 0.080 TO 0.025 INCH. X-ray spectrogram does not show doublets to be sharply resolved, because of reproduction of film. Photometer recording shows resolution of doublets, especially in higher orders. Note sharpness of peaks of doublets and how well resolved they appear on recording. Molybdenum radiation; zirconia filter; 0.020-in. slit system; angle of incidence,  $40^\circ$ ; 1152 ma-hr.

mentation does not go on without limit; in other words, the fragments cannot be made smaller than a certain definite size, no matter how severe the plastic deformation may have been.

The large-grained specimen, Fig. 7a, was cold-rolled from 0.048 to 0.017 in. and examined by this method. It is shown because of the unusual sharpness of the (211) lines, and is by far the best one made from the standpoint of reproduction. The  $(211)_2$  line is sharply resolved and of great intensity. The other lines were also sharply resolved but are not as intense as this particular line.

The X-ray diffraction diagram shown in Fig. 7b is of unusual interest in that the cold-rolled and heat-treated diagrams are superimposed on the same film. One can easily observe that the coincidence of the lines due to the cold-rolling and annealed structures is exact. To appreciate this one must examine the negative. The slightest deviation of the line position would have blurred the  $K_{\alpha_1}$  and  $K_{\alpha_2}$  lines of the doublet. This result can only be interpreted to mean that plastic deformation does not change the dimensions of the space lattice.

In the next X-ray diffraction diagram the effect of cold-working on the line structure will be investigated. Fig. 8 is the X-ray reflection diagram made of the 0.90 per cent C strip steel that was cold-rolled from 0.082 to 0.025 in. To resolve the lines, it was found necessary to use a larger angle of incidence, and  $40^\circ$  was found to be satisfactory for the 0.020-in. slit system. As the particle size becomes smaller and smaller, the difficulty in resolving the doublets sharply increases, and for this reason the angle of incidence was increased.

The X-ray diagram does not show clearly the  $K_{\alpha}$  doublets resolved and for this reason a photometer recording was made of this film. The  $K_{\alpha}$  doublets are resolved and the line width was found to be correct for the slit system used. This X-ray spectrogram was made with the largest slit system. A much better diagram could have been obtained with a slit system having smaller apertures, but this does show one thing clearly—that the particle size of a high-carbon steel is smaller than of a low-carbon steel given the same reduction. The hardness of the 0.90 per cent C steel after cold-rolling was about Rockwell C/−30.

#### DISCUSSION OF RESULTS

The results of this investigation are in excellent agreement with the theory proposed by Jeffries and Archer.<sup>11</sup> The increase in hardness can be explained as due to mechanical refinement of the grains by cold-working without assuming the necessity of lattice distortion. The extent to which a metal can be hardened depends only upon the extent of fragmentability of the crystalline structure.



It is believed in view of the evidence presented here that line broadening observed by other investigators, and considered by them as essentially due to lattice distortion, was due to broadening of the X-ray beam by the diffracting particle, since a divergent beam is broadened by particle sizes in this range and a nearly parallel beam is not, provided it is diffracted at the proper angle of incidence from the surface of the specimen.

If line broadening had been essentially due to lattice distortion it would not have been possible to resolve the  $K_\alpha$  doublets, even by the most refined X-ray technique. It has been shown by many investigators that the particles are never smaller than  $10^{-5}$  cm. and it is well known that such sizes should yield sharp lines since they are well above the colloidal range.

Another interesting fact found by these experiments was that in some instances the  $K_\alpha$  doublets could be resolved sharply without resorting to extreme refinements, while in others the best possible conditions had to be employed in order to obtain sharp  $K_\alpha$  doublets. This means that, depending upon the nature of the metal or alloy, cold-working causes wide variations in the particle size, and this determines the physical properties to a substantial degree.

The position taken on the basis of the experimental data gathered over the past eight years, and covering hundreds of cold-rolled specimens, is that cold-working does not distort the space lattice but merely refines the grains into smaller particles—the limiting size of which depends upon many factors. The most drastic cold-working cannot fragment the grains beyond about  $10^{-5}$  cm. in magnitude.<sup>15</sup>

The X-ray method used in this investigation is precise enough to detect any changes in the lattice parameters of the cold-worked alpha iron, required to account for decrease in density. (It must also be remembered that the broadening of the  $K_\alpha$  doublet has always been considered a sensitive test for slight variation in line position.) Another fact believed to support the position taken on the basis of this experimental work is that the photometer curves did not show any increase in the width of the  $K_{\alpha_1}$  and  $K_{\alpha_2}$  lines.

It is also well known that the most drastic cold-working will not harden a metal beyond a certain hardness value and that usually it can be made much harder by other means. The relationship between the reduction in thickness and hardness is shown in Fig. 9. At first the hardness increases very rapidly for reductions up to 30 per cent. In this interval the fragmentation is proceeding rapidly. The increase in hardness in the range 30 to 80 per cent is less marked and increases very slowly in the interval of 80 to 95 per cent. At 95 per cent the crystal break-up has practically reached its limit for it is difficult to detect a further increase in the hardness beyond 95 per cent.

It seems reasonable to assume that reductions up to 10 per cent break the grains into fragments that are fairly large but quite uniform in size.



With continued deformation the average size of the grain fragments is progressively decreased and finally reaches a size beyond which further break-up is not possible and no further increase in hardness can be detected.

It has also been assumed by some investigators that the extent to which a metal can be hardened by cold-working is limited by the intensity of the orientation texture. If the viewpoint taken here is correct the limiting hardness would depend to a greater degree on the extent to which the fragmentation can be carried. If the metal or alloy could be worked so that the crystal fragments would approach colloidal dimensions much greater hardness values could be attained.

It is also well known that cold-working decreases the density of a metal. This has been explained as being due to slight increase in the dimensions of the space lattice. In view of the results obtained in this experiment the decrease in the density cannot be explained on the basis of lattice distortion, and must be accounted for on other grounds.

The decrease in density of a metal can also be explained by assuming a large increase in the internal surface. This demands a slight increase in the spacing of the displaced lattice fragments caused by the rotation of the lattice fragments relative to each other. This concept is not new; it is only an extension of a well established experimental fact that a large single crystal has maximum density and polycrystalline aggregations have less density. Maier<sup>10</sup> has experimentally determined the density of various metals and for copper his results are as follows:

DENSITY	GRAIN SIZE
8.95285	Single crystal
8.94331	Fine grain—annealed
8.92018	Cold-rolled, 45.5 per cent
8.91186	Cold-rolled, 58.0 per cent

There is a gradual decrease in the density as the particle size becomes smaller and smaller.

The results and interpretations offered here are in good agreement with the observed fact that a lattice expansion would require a decrease in the specific heat capacity, but in cold-worked metals the heat content is increased slightly, as pointed out by Maier on page 36 of his article. The decrease in density and increase in the heat capacity can be explained by an increase in internal surface. Other physical properties also can be explained on this theory. It is apparent that the changes in the physical

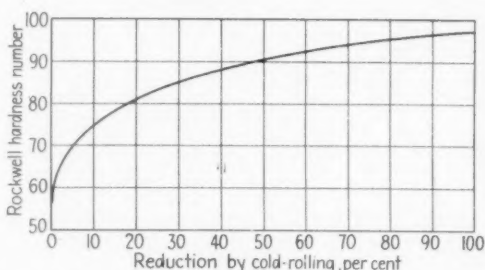


FIG. 9.—HOT-ROLLED STRIP RIMMED STEEL; 0.112-INCH STRIP COLD-ROLLED TO VARIOUS GAUGES.

properties that occur when a metal such as alpha iron is cold-worked can be explained without resorting to lattice distortion.

#### SUMMARY

1. A new X-ray technique has been developed for the study of plastically deformed metals. The  $K_\alpha$  doublets can be sharply resolved by using a substantially parallel beam of X-rays diffracted by the surface at the proper angle of incidence. The smaller the grain fragments the more difficult it becomes to resolve the  $K_\alpha$  doublets and the better the X-ray technique must be.

2. Plastic deformation does not distort the space lattice of alpha iron but fragments the grains into smaller particles.

3. The decrease in density that accompanies cold-working can be explained by the increase in the internal surface due to new orientations created within the grain by grain fragmentation.

4. A single crystal has maximum density and all fine-grain annealed aggregates and fragments created by plastic deformation have a slightly lower density.

5. The hardening of a metal by cold-working can be explained as due to mechanical refinement of the grains into smaller ones differing in orientation from the parent grain, as proposed by Jeffries and Archer. The evidence presented is believed to support this theory.

6. The surface-diffraction diagrams also prove that cold-working does not fragment the grains without limit. Cold-working appears only capable of fragmenting the grains into particles about  $10^{-5}$  cm. in magnitude. (Recent work published by W. A. Wood supports this conclusion.)<sup>15</sup>

7. The study of the changes in physical properties of metals accompanying plastic deformation is important from a technical as well as a theoretical viewpoint. This investigation shows that these changes are due to changes in particle size and not to lattice distortion.

The study of particle size, then, becomes of the greatest importance. The X-ray method described can be used to determine with great accuracy the average particle size for any given plastic deformation. A small change in the particle size reduces the intensity of the lines of higher order and indices. By standardizing the experimental conditions particle-size determinations can be made easily.

#### ACKNOWLEDGMENT

The helpful assistance of Dr. H. A. Smith in suggesting revisions in definitions and terms, and in making a final review, is gratefully acknowledged.

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## DISCUSSION

(John T. Norton presiding)

C. A. ZAPFFE,\* Columbus, Ohio.—At Battelle Memorial Institute there is research in progress on the submicroscopic structure of metals. Results to date, though incomplete, agree with those presented by Mr. Goss in ascribing to metals a definite and an important submicroscopic structure. Some preliminary evidence has already been published<sup>16</sup> that relates hydrogen embrittlement to the fine structure of steel, and further work<sup>17</sup> has shown that several other well-known defects in steel can be explained simply as functions of submicroscopic crystallography.

Two questions may be raised in regard to the present work, however. First, metallic lattices in general are slow to attain equilibrium at ordinary temperatures and X-ray patterns therefore may be expected in some cases to show some diffuseness from lattice distortion. For example, palladium in iron may cause an expanded body-centered cubic lattice to form when rapidly cooled from temperatures above the critical.<sup>18</sup> The X-ray lines in the palladium-iron system are too far from alpha-iron positions to be accounted for as spread from the block structure, and their diffuseness is very likely due to true distortion of the iron lattice by palladium atoms that have been unable in the short quenching period to leave their gamma positions and form the equilibrium structure. Martensite reactions in general are of this type.

Secondly, the "proper angle of incidence" appears to be an important function in the present work that the author has not discussed. Unless explained, the critical nature of this angle might be taken by some as evidence that lattice distortion is the cause of the diffuseness in the patterns, and that clarity is obtained at certain angles because the distortion has been distributed preferentially in the rolling structure and is a minimum in the direction of the X-ray beam.

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<sup>16</sup> C. A. Zapffe and C. E. Sims: *Hydrogen, Flakes and Shatter Cracks. Metals and Alloys*.

<sup>17</sup> C. A. Zapffe and C. E. Sims: *The Mechanism of Flake and Shatter Crack Formation*. To be published shortly.

<sup>18</sup> R. Hultgren and C. A. Zapffe: *An X-ray Study of the Iron-palladium and Nickel-Palladium Systems. Trans. A.I.M.E.* (1939) **133**, 58.

A. GOETZ, \* Pasadena, Calif.—The results described in this paper furnish not only a definite proof that, at least for alpha iron, cold-hardening is *not* due to a plastic distortion within the lattice configuration of the metal atoms—i.e., within the “primary” structure—but gives also an explanation for the fact that the broadening of the lines has frequently been interpreted in terms of a lattice distortion due to the lack of resolving power by the apparatus employed.

The picture of progressive fragmentation of the large crystals into smaller, as such undeformed, fragments with increasing external deformation, seems to be in good agreement with the general theory of plastic deformation in metallic crystals originated by Taylor,<sup>19</sup> where the probability for progressive subdivision of the crystal by gliding and the consequent genesis of new internal surfaces is predetermined by statistical interatomic irregularities within the lattice distortions, for they cannot contribute to the diffraction pattern; and within a realm bordered by these dislocations the lattice could be neither fragmented into smaller particles nor could each fragment be deformed within itself. The smallest size is postulated by Taylor to lie between  $10^{-4}$  to  $10^{-5}$  cm., depending on the type of lattice. The former is in agreement with the magnitude of the “smallest etch figure,”<sup>20</sup> and has been observed for alpha iron by Belaiew<sup>21</sup> at  $2.5 \times 10^{-5}$  cm.; i.e., a magnitude that should not yet cause an appreciable broadening of the X-ray lines. The size of this undeformable lattice unit indicated by Mr. Goss’ work agrees in magnitude also well with the “critical” size of diamagnetic metallic crystals.<sup>22,23</sup>

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\* Cryogenic Laboratory, California Institute of Technology.

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<sup>20</sup> A. Goetz: *Proc. Nat. Acad.* (1930) **16**, 99.

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## Crystal Orientation in Silicon-iron Sheet

By J. T. BURWELL\*

(New York Meeting, February 1940)

THE crystal orientation in silicon iron that has been given a particular treatment described by Goss,<sup>1</sup> has been studied by Goss, by Bozorth<sup>2</sup> and by Sixtus,<sup>3</sup> but their results do not agree and are almost entirely qualitative. The following pages give a description of the orientation of the crystals in the material as determined by means of X-rays and expressed graphically in a pole figure.

The treatment consists of hot-rolling the material into strip and then giving it two cycles of cold reduction followed by recrystallization. This produces remarkably good properties in the rolling direction, the product having a maximum permeability in this direction of more than 25,000 and a permeability at 16,000 Gauss of more than 2200. It is now generally agreed that Goss's original conclusion<sup>1</sup> that the crystals in the final product are randomly oriented was incorrect, since Bozorth<sup>2</sup> and Sixtus,<sup>3</sup> using different methods, have shown that there is a decided preference in orientation. Those writers, however, expressed their results only in terms of one or more ideal orientations with deviations therefrom.

### X-RAY DATA

A strip of the material containing 3.1 per cent Si, prepared by Goss,† 1.2 by 0.0125 in., was etched rapidly in warm dilute hydrochloric acid until it was 0.005 in. thick, in order to eliminate the effect of the two surface layers. The specimen was then mounted in an integrating camera similar to one described in the literature.<sup>4</sup> The purpose of this camera is to translate the specimen during exposure, so that a statistically large number of grains contribute to the pattern photographed. The camera also allows the plane of the specimen to make various angles with the X-ray beam. An area 5 by 1.2 in. was scanned by a beam of unfiltered radiation from a molybdenum target tube operating at 37 kv., and the measurements were made principally on the peak of the white radiation. X-ray photographs were taken at intervals of 15° in a plane

Manuscript received at the office of the Institute Dec. 1, 1939. Issued as T.P. 1178 in METALS TECHNOLOGY, February 1940.

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<sup>1</sup> References are at the end of the paper.

† The author is indebted to Prof. L. W. McKeehan for the sample of this material used in the present work.



perpendicular to the rolling direction, and one was taken with the beam rotated  $7^\circ$  from the normal to the sheet toward the rolling direction.

### RESULTS AND DISCUSSION

Two representative photographs are shown in Fig. 1. From the several photographs a pole figure (Fig. 2) was constructed, showing the density of  $[110]$  poles. The small diamonds indicate the positions of the  $[110]$  poles of a single crystal oriented so that a  $(110)$  plane lies in the rolling plane and a  $[001]$  axis in the rolling direction. This figure shows that, in agreement with Bozorth, who also used X-rays, the majority

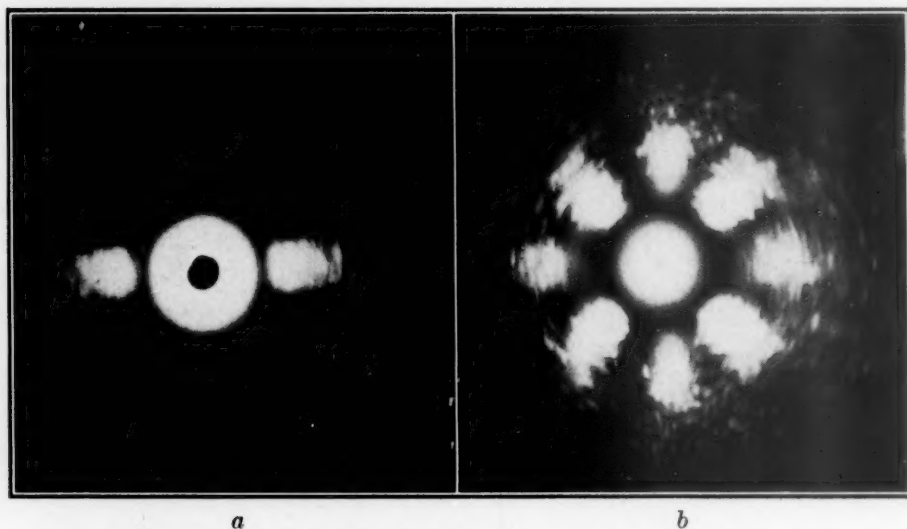


FIG. 1.—GOSS MATERIAL, ROLLING DIRECTION VERTICAL.  
*a*, beam normal to strip.  
*b*, beam  $90^\circ$  from rolling direction and  $45^\circ$  from normal to strip.

of the crystals deviate from the orientation indicated by the diamonds in Fig. 2 by less than  $11^\circ$  toward the rolling direction or cross direction and by not more than  $20^\circ$  from the cross direction in the plane of the strip. There is, however, a slight density of  $[110]$  poles pointing in almost every direction. This is also in agreement with the results of Sixtus,<sup>3</sup> who, by analysis of magnetic torque curves of this material by the method of Akulov and Brüchatov,<sup>5</sup> concluded that about two-thirds of the crystals have the single crystal orientation described above. On the other hand, he found, by an optical etch-pit method, that in addition to the orientation described there was another group of crystals, amounting to almost one-half the total number of crystals, oriented so that a  $(100)$  plane lay in the rolling plane and a  $[001]$  axis in the rolling direction. Zaimovski and Kazarnovski,<sup>6</sup> on the basis of magnetic torque measurements, have also reported this second type of orientation. In the pole figure of Fig. 2, there is little trace of the latter orientation except for the low isthmus connecting the two nonequatorial islands of large density, but

this could hardly correspond to half of all the crystals in the specimen. There is no obvious explanation of this discrepancy.

It might be interesting to compare these results with those on silicon-iron alloys at various stages in their processing. Frey and Bitter<sup>7</sup> state that each cycle of cold reduction followed by recrystallization serves to increase the percentage of crystals having a (110) plane in the rolling plane and a [001] axis in the rolling direction, and to decrease the percentage having a (100) plane in the rolling plane and a [011] axis in the rolling direction. The present work, when taken in conjunction with that of Barrett, Ansel and Mehl,<sup>8</sup> seems to be in agreement with this statement. Figs. 7 and 8 of their paper<sup>8</sup> are pole figures of silicon-iron alloys that have

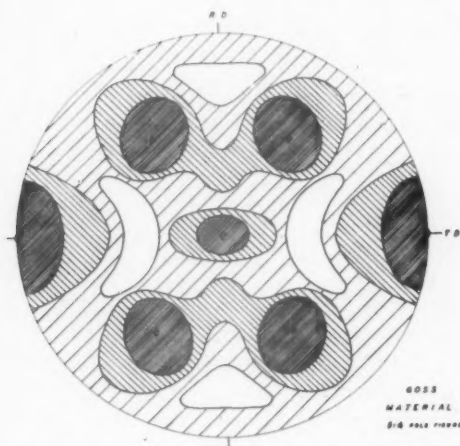


FIG. 2.—[110] POLE FIGURE FOR GOSS MATERIAL.

Plane of sample in plane of paper and rolling direction vertical.

Small diamonds indicate positions of [110] poles of single crystal oriented so that a (110) plane lies in rolling plane and a [001] axis in rolling direction.

been cold-rolled 95 per cent; they show that most of the crystals are oriented with the [011] axis in the rolling direction, and while there is some spread in rotation of the crystals around this direction the majority have a (100) plane in or near the rolling plane. Their Figs. 17, 18 and 19 are pole figures of silicon-iron alloys that have been cold-reduced 95 per cent and then recrystallized. These show some similarities to the cold-rolled figures but also a great many differences, the principal one being that the [011] axis no longer lies in the rolling direction but in most crystals is rotated in the rolling plane  $17^\circ$  to one side or the other. This may be considered as a transition structure. Fig. 2, made from a material that was twice cold-reduced and recrystallized, shows crystals oriented with a (110) plane in the rolling plane and a [001] axis in the rolling direction.

#### SUMMARY

The results of an X-ray examination of silicon iron prepared by the process of N. P. Goss are expressed in the form of a pole figure; they

indicate that the component crystals are oriented with a (110) plane in the rolling plane and a [001] axis in the rolling direction. This is in agreement with the results of Bozorth and with the magnetic results of Sixtus but not with those of the optical method used by the latter, nor with Goss's original conclusions.

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## DISCUSSION

(S. L. Hoyt presiding)

N. P. Goss,\* Youngstown, Ohio.—The author has shown by means of a pole figure that the high permeability of silicon strip steel made according to the "Goss process" can be obtained only when the grains deviate but slightly from the orientation previously described by Bozorth. As the grains deviate more and more from the desired orientation the magnetic properties become increasingly inferior.

The torsion magnet was used by the writer in developing this process, and it was found that when a high percentage of the grains are oriented as described by Burwell the torque curve of the fine-grained strip would nearly coincide with the torque curve of a single crystal, as shown in Fig. 3.

These unusual magnetic properties can be attained only when the silicon strip steel is processed according to the method described in a previous paper.<sup>9</sup>

Silicon strip steels rolled directly to gauge and heat-treated have several other undesirable orientations present, in addition to the desirable orientation. It is, to say the least, surprising to find even in inferior cold-reduced silicon strip a good percentage of the desired orientation, but this is modulated by the other undesirable orientations.

The following orientations are usually present in varying degrees in ordinary heat-treated cold-reduced silicon strip steel:

In Rolling Direction	Transverse to Rolling Direction	In Surface of Strip
[100]	[110]	(110)
[110]	[110]	(100)
[110] or [211]	[211]	(211)

\* Director of Research, Cold Metal Process Co.

<sup>9</sup> N. P. Goss: New Development in Electrical Strip Steels. *Trans. Amer. Soc. Metals* (1935) **23**, 511.

L. P. TARASOV,\* Schenectady, N. Y.—By means of a thorough X-ray study, Dr. Burwell has been able to show clearly that the predominant texture in silicon iron prepared by the Goss process has the (110) plane in the rolling plane and the [001] direction in the rolling direction; and that the additional texture described by other investigators, in which (100) and [001] are supposed to be in the rolling plane and direction, respectively, is definitely absent. Although this second texture was proposed on the basis of two distinct methods, the evidence in its favor is very weak compared to the X-ray evidence against it.

One of these methods, involving magnetic torque measurements, is incapable by itself of proving that the second texture exists. The trouble is not with the torque data but with their analysis, which was carried out by the highly artificial method of Akulov and Brüchatov. For this type of analysis to hold, it must be assumed that some of the grains are all oriented one particular way with no appreciable deviations therefrom, that some others are all oriented another way, and that the rest are oriented at random. In such a case, it tells exactly what fraction of the grains is oriented in each of the three ways. But if there are any considerable deviations from the mean

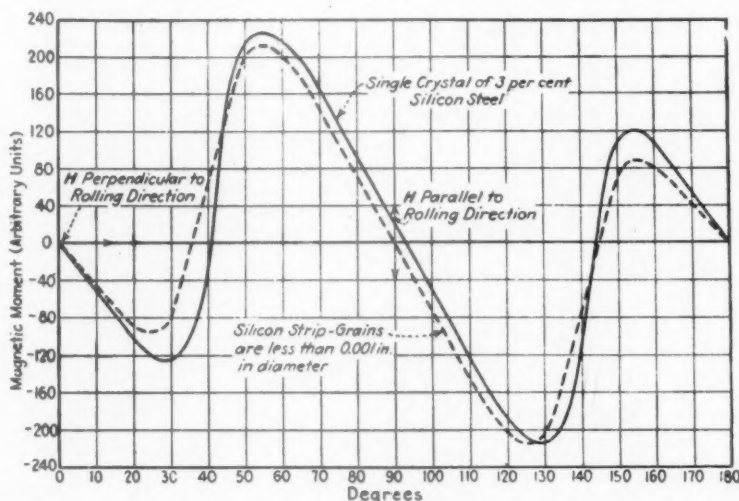


FIG. 3.—TORSION MAGNETIZATION CHARACTERISTICS OF GOSS SILICON STEEL CONFORM CLOSELY WITH THE CHARACTERISTICS OF A LARGE SINGLE CRYSTAL. SEVERAL SILICON STEEL SPECIMENS HAVE DISPLAYED A MAGNETIC MOMENT EVEN GREATER THAN THAT SHOWN HERE FOR A SINGLE CRYSTAL.

Reprinted from *Iron Age*, Feb. 21, 1935.

orientations, and this always happens in practice, the foregoing analysis may lead to erroneous conclusions. Some time ago, I discussed this point in greater detail in connection with the texture of cold-rolled iron,<sup>10</sup> and showed that even in this simple case an analysis according to this method gave the wrong result. Thus the torque data cannot serve as proof of the second texture. It should be stressed that magnetic torque studies are useful if interpreted properly but that this particular type of analysis of the torque data is not justified.

This leaves the results of the optical etch-pit method as the only evidence for the second texture. Although this method can be made very accurate and reliable, as described by Barrett and Levenson,<sup>11</sup> it is possible to be led astray if certain precau-

\* Research Laboratory, General Electric Co.

<sup>10</sup> L. P. Tarasov: *Jnl. Applied Physics* (1938) **9**, 192.

<sup>11</sup> C. S. Barrett and L. H. Levenson: Determination of Orientations by Etch Pits. *Trans. A.I.M.E.* (1940) **137**, 76.

tions are not taken. As used by Sixtus, this method was only a rough one and perhaps some of the pits produced by his etching technique were misinterpreted. It is difficult to explain how a hypothetical second texture could have been missed so completely by X-rays. Since the optical results obviously are more open to question than the X-ray results, the most logical thing to say under these circumstances is that the second texture has not yet been proved to exist. It would certainly be interesting to repeat the optical work on the same material, using the more refined technique developed by Barrett and Levenson.

J. T. BURWELL (author's reply).—Mr. Goss' comments are much appreciated but it should be pointed out that the first paragraph of his remarks is a conclusion of his own and not of the author's. In the present paper it is shown that silicon-steel strip made according to the "Goss process" has the grain orientation shown in Fig. 2 but the magnetic properties of this material were not reported. Mr. Goss's remarks about the extreme dependence of magnetic properties on grain orientation are most interesting, but it should be borne in mind that the concomitant changes produced by any particular method of processing on other properties of the material, such as its composition or freedom from strain, may result in even disproportionately larger changes in permeability and core loss.

Dr. Tarasov's discussion of the various methods employed for the determination of crystal orientation reveals a possible explanation of the discrepancy noted between the results of the present work and those of others, but the author agrees that the optical etch-pit method should be repeated on this material to clear up this point.



## Some Observations on the Recrystallization of an Iron-nickel Alloy

BY GEORGE SACHS,\* MEMBER A.I.M.E., AND J. SPRETNAK†

(New York Meeting, February 1940)

THE process of recrystallization has not as yet been explained satisfactorily. Some definite conclusions could be drawn from recent investigations, such as, for example, that recrystallization is a process of nucleus formation and crystal growth<sup>1</sup> and that the orientations of the nuclei correspond to some fragments of the original crystals, which have been considerably distorted during deformation.<sup>2</sup>

There are, however, a number of metals and alloys crystallizing in the face-centered cubic system, which form a particularly simple orientation if recrystallized as a sheet.<sup>3</sup> Such a sheet is almost a single crystal with the cubic axes parallel to the rolling, transverse, and normal directions of the sheet. This preferred cubic or (100) orientation of the recrystallized sheet has been considered to be very different from the rolling structure of the same metals,<sup>4</sup> but there are two reasons why this last supposition remains open to controversial discussion.

The first reason is academic: In practically all cases except the one mentioned above, close correlations and similarities between rolling and annealing orientations have been observed; for instance, in iron and steel sheet.<sup>5</sup>

Secondly, no deformed metal actually forms a simple orientation. In any thoroughly investigated case a number of different orientations and considerable scattering or deviations from the ideal orientations have been found.<sup>6</sup> It is generally true that investigations on single crystals have shown that a definite orientation is approached in stretching or in compression of an originally undisturbed crystal.<sup>7</sup> In the special cases, however, where the initial orientation was close to an important crystallographic direction that differed from the final "ideal" orientation, the resulting orientation changed very little by deformation, staying somewhere in the vicinity of the initial orientation.<sup>8</sup> Such deviations

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Manuscript received at the office of the Institute Oct. 27, 1939. Issued as T.P. 1143 in METALS TECHNOLOGY, January 1940.

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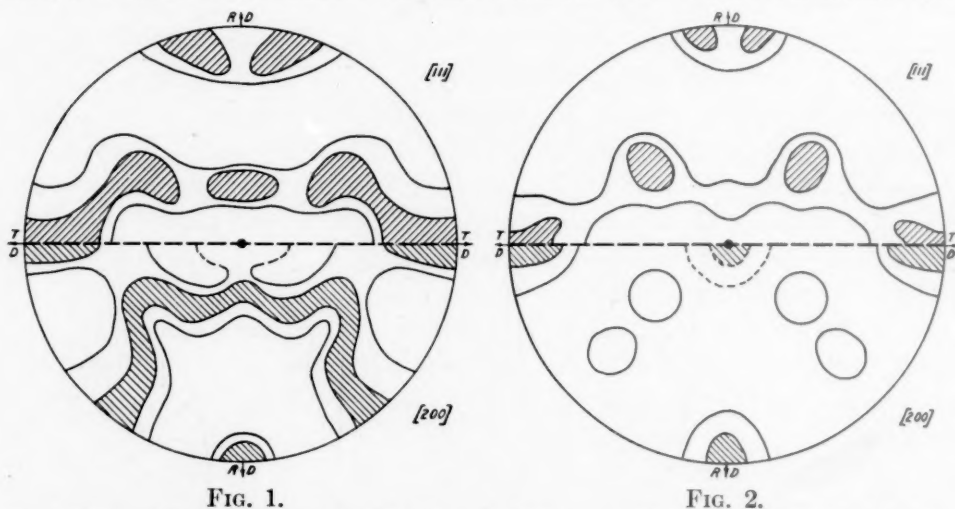
<sup>1</sup> References are at the end of the paper.

from a simple and definite orientation should be more pronounced in a polycrystalline metal subjected to a commercial working. The varying conditions in working processes probably explain also the many differences in details that have been observed by various workers in investigations on the same metals deformed by rolling.

As an attempt to clarify this inconsistency in our present theories of recrystallization—namely, the formation of an orientation on annealing that differs entirely in type from that of the rolling structure—the rolling and recrystallization structures of a metal that forms a cubic structure on recrystallization have been investigated again with the special purpose of detecting a correlation between these two structures.

#### EXPERIMENTAL PROCEDURE

Since it had been reported by German investigators<sup>9</sup> that iron-nickel alloys with a high nickel content formed the "cubic structure" on



FIGS. 1-2.—POLE FIGURES FOR (111) (ABOVE TD) AND (200) (BELOW TD) PLANES OF IRON-NICKEL SHEET (64 PER CENT IRON, 36 PER CENT NICKEL).

Fig. 1. Rolling structure. Reduced 95 per cent by rolling.

Fig. 2. Annealing structure. Rolled 95 per cent, annealed  $\frac{1}{2}$  hr. at 900° C. and additionally rolled 10 per cent.

recrystallization after heavy deformation by rolling, an austenitic iron-nickel alloy containing approximately 36 per cent nickel was selected for this investigation. The analysis of the alloy is given as: 35.64 per cent Ni; 0.04 to 0.08 Si; 0.17 to 0.20 Mn; 0.02 C; 0.006 P; 0.020 S; balance Fe. The alloy was prepared by the Research Laboratories of the International Nickel Co. at Bayonne, N. J.

The alloy, after a pre-anneal, was rolled from a piece approximately 3 by  $\frac{7}{16}$  by  $\frac{3}{8}$  in. to the final sheet. A 95 per cent reduction was obtained by 30 to 40 passes on an 8 by 11-in. two-high mill. Although the conditions of rolling were not controlled to any great extent, the final structure and results obtained proved them adequate for this particular



FIG. 3.

FIG. 4.

FIG. 5.

FIGS. 3-5.—X-RAY DIFFRACTION PHOTOGRAPHS OF IRON-NICKEL SHEET.  
 Fig. 3. Reduced 95 per cent by rolling.  
 Fig. 4. Rolled 95 per cent and annealed  $\frac{1}{2}$  hr. at  $900^{\circ}$  C.  
 Fig. 5. Rolled 95 per cent, annealed  $\frac{1}{2}$  hr. at  $900^{\circ}$  C. and additionally rolled 10 per cent.

investigation. The metal was investigated in three conditions: (1) cold-rolled, 95 per cent reduction; (2) then annealed 30 min. at 1750° F. (900° C.), (3) then (after annealing) cold-rolled, 10 per cent reduction.

The third condition was taken as a complete determination of the orientation of the annealed specimen because it gave more satisfactory photograms for measurement than did the pictures of condition 2, which were complicated by the presence of individual spots, characteristic of patterns of recrystallized metals. The additional small reduction after annealing was justified, as it had been reported<sup>9</sup> that the "cubic structure" is retained on further rolling up to 50 per cent reduction.

The specimens examined were cut from the rolled strip, which was about  $\frac{1}{2}$  in. wide, to an approximate  $\frac{1}{2}$ -in. square section, so that the rolling, transverse, and normal directions were parallel to the three edges of the sheet. The original thickness of 0.017 in. was reduced to between 0.001 and 0.002 in. by pickling in a mixture of nitric and hydrochloric acids in order that transmission X-ray photograms might be taken of the sheet. The pickling was advantageous also in that it removed the complication of the outside layers, which have generally a structure different from that of the inside portion.<sup>5</sup> The data presented here, therefore, apply only to the inside structure.

The transmission photograms were taken with a General Electric X-ray diffraction unit equipped with a molybdenum target tube. Rotation of the sheet in steps of 5° to 15° was accomplished by the use of a goniometer head. The rotations made were in two directions—about the rolling direction and about the transverse direction. The angular range covered was 0° to 70° in both directions. Between 70° and 90° only a few reflections were observable, so that this region was not thoroughly covered. Ten to twenty exposures at short intervals were made of each specimen. The intensity of the reflections was estimated visually and first and second order intensities were plotted.

From these X-ray photograms the so-called "pole figures" (Figs. 1 and 2) were constructed for the two principal planes, the (111) or octahedral plane and the (100) or cubic plane. The (111) and (200) reflections of a face-centered metal or alloy correspond to the innermost circles in the X-ray photograms. The annealed metal (condition 2) is not represented because its pole figures were practically the same as that of the annealed and 10 per cent reduced (condition 3) specimen. Figs. 3 to 5 show the photograms of the three conditions with the X-ray beam perpendicular to the sheet.\* This evidence substantiates the previously

\* Figs. 4 and 5, representing conditions 2 and 3, respectively, appear at first sight somewhat different. A closer examination, however, reveals that the X-ray patterns are much alike, and the pole figures show that the apparent differences result from a slightly larger amount of the rolling structure and scattering in condition 3 than in condition 2.

mentioned report that the cubic structure is retained on further reduction after annealing.

### RESULTS

The pole figures for the rolled metal (Fig. 1) are similar to previously published pole figures for other face-centered cubic metals; for instance, the particularly often investigated metal aluminum (Fig. 6). The rolling structure of the iron-nickel alloy can be explained for the major part as in the case of many other face-centered cubic metals,<sup>4</sup> by a superimposition of two orientations, designated as (111) and (112), which are illustrated in Fig. 7. There is, however, one important difference as compared with the aluminum structure. The pole figure in the present case contains some regions that have not been observed or reported in previous

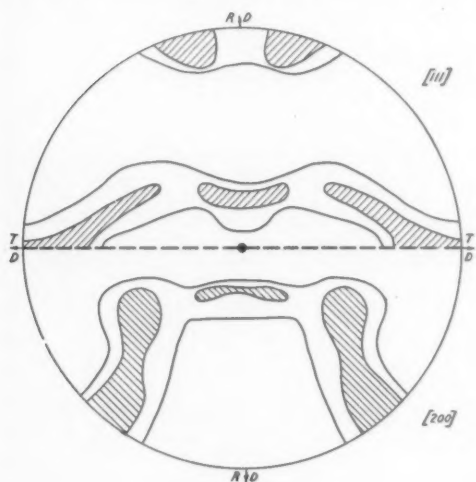


FIG. 6.

FIG. 6.—POLE FIGURE FOR (111) AND (200) PLANES OF ROLLING STRUCTURE OF ALUMINUM. (v. Göler and Sachs.)

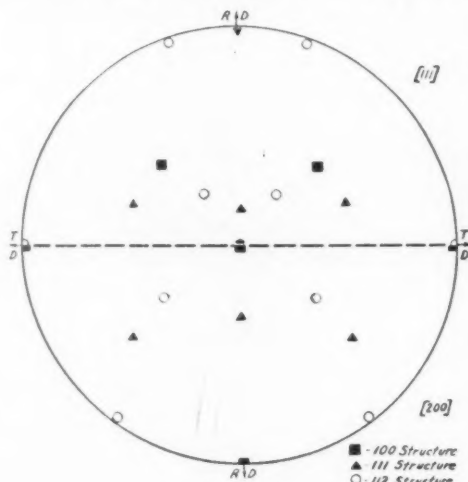


FIG. 7.

FIG. 7.—IDEAL CRYSTAL ORIENTATIONS IN ROLLED AND ANNEALED SHEETS OF FACE-CENTERED CUBIC METALS.

investigations. These additional regions can be accounted for by the presence of crystals in the cubic orientation (Figs. 1 and 7). In Fig. 7 the respective locations of the crystallographic planes (111) and (100) are given for three orientations, which make up the major parts of both

TABLE 1.—Structure of Iron-nickel Alloy

Orientation	Direction of Sheet		
	Rolling	Transverse	Normal
(100)	[100]	[010]	[001]
(111)	[111]	[110]	[112]
(112)	[112]	[111]	[110]



the rolling and annealing structure for the iron-nickel alloy. These orientations can also be described as in Table 1.

Thus in the iron-nickel alloy undoubtedly crystal fragments in orientations corresponding to the recrystallized structure are already present to a certain extent in the rolled material. The formation of the cubic orientation on recrystallization therefore may be attributed to the phenomenon of such fragments (in the cubic position) being particularly favored to form nuclei on recrystallization and having the capacity to absorb nuclei and crystals of other orientations.

The observations on the recrystallized metal confirm these conclusions. At the lowest investigated annealing temperature of 1110° F. (600° C.) at which recrystallization had taken place, a considerable amount of the

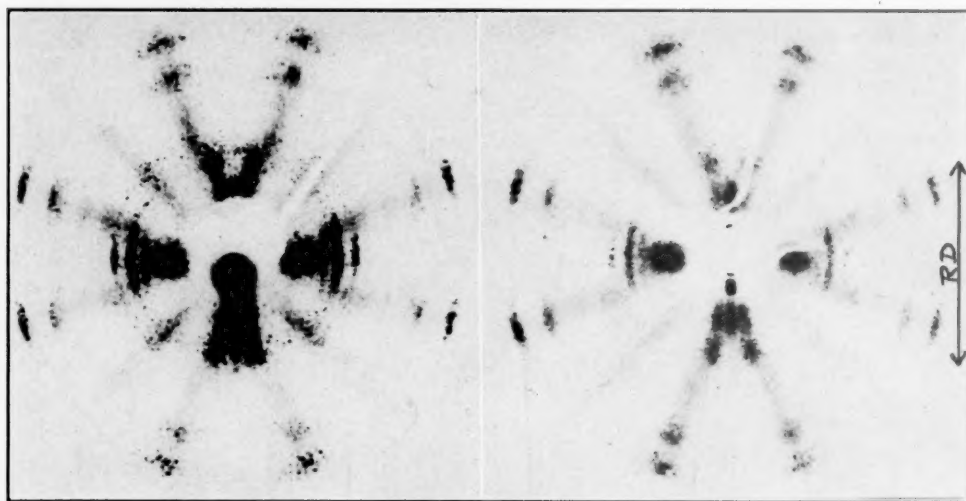


FIG. 8.

FIG. 9.

FIGS. 8-9.—X-RAY PHOTOGRAMS OF ROLLED AND ANNEALED IRON-NICKEL SHEET.

Reduced 95 per cent by rolling and annealed  $\frac{1}{2}$  hr. at 600° C. and 800° C., respectively.

rolling structure was retained, as can be concluded from Fig. 8. With increasing temperature the cubic structure becomes more and more pronounced (Figs. 4 and 9), but at 1750° F. (900° C.), a certain portion of the crystals may still be found in the positions of the principal rolling structure, according to the pole figures of Fig. 2. The deviations in Fig. 2 from the simple cubic structure correspond closely to the (111) and (112) orientations (Fig. 7) that compose the major part of the rolling structure (Fig. 1).

#### CONCLUSION

It may be concluded from the reported experiments that the process of recrystallization in this particular case is consistent with the theory that the process is initiated by some specifically oriented fragments of the

deformed metal. These fragments, for a still unknown reason, are more favored to form nuclei, to grow on recrystallization, and to survive on grain growth\* than the remainder of the deformed metal.

### SUMMARY

1. The rolling and annealing structures of a relatively pure iron-nickel (36 per cent) alloy were investigated by X-rays to detect possible correlation between the two structures.

2. Pole figures for the rolling structure were found to be similar to those of other face-centered cubic crystallized metals—as, for example, aluminum—and were explained for the major part by superimposition of (111) and (112) structures.

3. Additionally, the hitherto unreported presence of a certain amount of the cubic structure in the rolled sheet was detected.

4. The pole figures of the annealed and the annealed plus 10 per cent reduced samples showed mainly the cubic structure, with some remaining rolling structure in evidence.

### ACKNOWLEDGMENTS

The authors are indebted to Dr. Paul D. Merica and Mr. A. J. Miller, of the International Nickel Co., for furnishing the alloy used in the investigation, and also its chemical analysis.

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### DISCUSSION

(S. L. Hoyt presiding)

C. S. BARRETT,† Pittsburgh, Pa.—If a nucleus of a recrystallized grain is as small as 10,000 Å. ( $10^{-4}$  cm) and grows to 0.2-mm. diameter, it grows 200 times in diameter, or 8 million times in volume. If a nucleus is only  $1/10$  this size ( $10^{-5}$  cm.) its growth is

\* It appears that these conditions of stability change at very high temperature when exaggerated grain growth starts and different orientations may be formed.<sup>9</sup>

† Metals Research Laboratory, Carnegie Institute of Technology.

1000 times that figure ( $8 \times 10^9$ ), and perhaps the nuclei are still smaller. What chance has an experimenter of seeing by X-rays, then, the minute fracture of the total volume that constitutes the nuclei—say  $10^{-7}$  to  $10^{-10}$ —of the whole? And what conclusions can be drawn from correlations between deformation and recrystallization textures?

The X-ray pictures show the matrix that serves as *food* for the nuclei, not the nuclei themselves. Probably there are enough scattered fragments of all orientations so that there would be nuclei available for any recrystallization orientation that we might want to explain, for all diffraction patterns have a background of low intensity between the intensity maxima.

The pole figures presented here indicate that there is merely a change in the intensity of the three principal orientations of the rolling texture upon recrystallization. Many will take this to mean that many fragments of the cold-rolled material retain their orientation on recrystallization, but this is not necessarily true. In fact, we have found the reverse to be true in aluminum after compression—a *change* in orientation for the bulk of the material in each fragment seems to be the rule. Probably only minute nuclei having the “right” orientation retain their orientation and devour relatively immense quantities of differently oriented material during the recrystallization process.

P. A. BECK,\* Perth Amboy, N. J.—Some years ago Burgers made an attempt to explain the preferred orientation in recrystallized metals by assuming preferred orientation of the nuclei produced by the deformation process. On the other hand, Dr. Barrett suggests that in the worked material there are a large number of nuclei present with a very wide variety of orientations and that the preferred orientation of the recrystallized structure results from the preferential growth of the nuclei near to a certain orientation. It may be of some interest in this connection to recall an observation made some years ago on the recrystallization of bent aluminum single crystals.<sup>10</sup> It was found that at a certain orientation and within certain limits of deformation, the bent matrix did not form nuclei by itself, although it was capable of being consumed by undeformed new crystals when it was “inoculated” with “artificial nuclei.” The artificial nucleation process produced a very large number of nuclei growing to small equiaxed crystals of a few tenths of a millimeter diameter, all situated in the immediate vicinity of the inoculating scratch. The rest of the recrystallized layer of the bent crystal usually consisted of only one large grain, surrounding the small crystals of the scratch. This phenomenon was interpreted as the result of selective growth of a crystal of a certain orientation. The alternative explanation, on the basis that the victorious nucleus was formed earlier than the others, seemed to be excluded, since otherwise the rest of the nuclei could not have had a chance to become active.

G. SACHS (authors' reply).—I do not understand Dr. Barrett's remark that the nuclei in a metal ready to recrystallize are too small to determine the final structure. There is general agreement at the present time that the recrystallization is a statistical phenomenon and that crystal fragments of any orientation have a certain chance to become stable nuclei and to grow. The number of nuclei within a small range of orientations will depend upon their relative rate of nuclei formation, and this in turn may be determined by various factors such as the volume of deformed metal within this orientation range, some unknown condition of internal strain and the possibility of twin formations. The final structure, furthermore, will be affected by the rate of crystal growth into the deformed matrix.

\* Central Research Laboratory, American Smelting and Refining Co.

<sup>10</sup> *Trans. A.I.M.E.* (1937) **124**, 362.

It is not necessary or even probable that a crystal of a certain orientation results from a deformed region of the same average orientation. On the contrary, according to the nature of a statistical process, no definite relation can be expected; but an approximate relation would exist between the *average orientations* of a large number of new crystals and the deformed matrix. Besides, in a statistical process, any possible orientation may be expected, occurring with a low frequency, so that the probable recrystallization structure should always consist of an at random orientation with a number of peak frequencies of varying magnitudes. Only the very frequent peaks have been generally determined; but the more extensive an investigation is being carried out, the more "orientations" have been found to be assembled in a specific deformation structure.

In regard to Mr. Beck's discussion, I would like to add that there is always some competition between the formation of a new nucleus and the invasion of neighboring crystals. This competition also determines in ingot solidification whether the crystals formed will be columnar or equiaxed.

## Magnetic Analyses of Transformations in a Cold-worked 18-8 Alloy

By R. BUEHL,\* H. HOLLOMON,† AND JOHN WULFF,‡ MEMBER A.I.M.E.

(Chicago Meeting, October 1939)

ALTHOUGH the main features of the transformations occurring in 18-8 have been published already,<sup>1-4</sup> certain conclusions merit questioning and discussion. The questions may be summarized as follows:

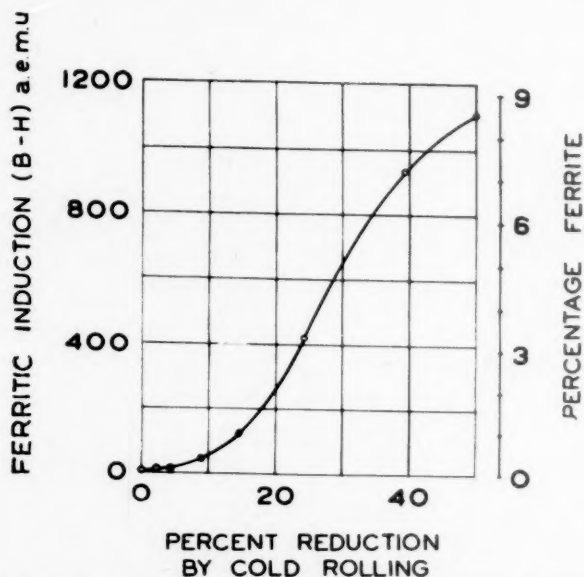


FIG. 1.—VARIATION OF FERRITIC INDUCTION AND PERCENTAGE OF FERRITE WITH COLD REDUCTION.

Composition of Alloy: C, 0.08; Mn, 0.40; Si, 0.24; P, 0.014; Cr, 18.13; Ni, 8.94.

1. If ferrite is formed by cold-working austenite, what happens to the carbon with which the ferrite and austenite are both presumably supersaturated?

2. What is the nature of the alpha-ferrite formed at grain boundaries by chromium-carbide precipitation at these boundaries?

Manuscript received at the office of the Institute July 14, 1939; revised Aug. 28, 1939. Issued as T.P. 1120 in METALS TECHNOLOGY, October 1939.

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† Student, Massachusetts Institute of Technology.

‡ Associate Professor of Physical Metallurgy, Massachusetts Institute of Technology.

<sup>1</sup> References are at the end of the paper.



3. Is the percentage of ferrite present in a cold-worked alloy increased by heating at temperatures up to 400° C. as previous magnetic measurements seem to show?

### EXPERIMENTS

The results reported in this paper are part of an investigation carried out on various 18-8 alloys, but this paper reports only the results that

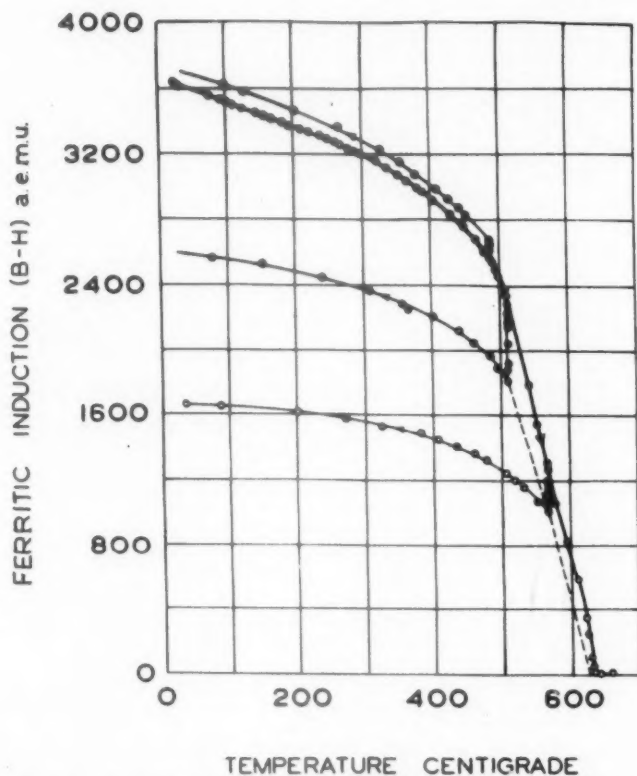


FIG. 2.—VARIATION OF FERRITIC INDUCTION DURING HEATING AND COOLING. SAME ALLOY AS IN FIG. 1.

Sample A. Annealed, quenched and cold-reduced by hammering, 83 per cent.

bear on the foregoing questions or supplement work previously obtained by others using the same or different techniques. The data have been obtained mainly by magnetic-moment measurements made, during heating and cooling, on a series of samples with different percentages of ferrite produced by cold-rolling.

The torsion balance and associated electromagnet used in the investigation have been described elsewhere<sup>5</sup> in detail. With this device, the force exerted on a small specimen suspended by a torsion fiber is measured between the poles of a strong electromagnet. The specimen is heated by a noninductively wound furnace, which surrounds it. If the magnetic field strength is sufficiently high to saturate the sample, the force is

$$F = \frac{\partial H}{\partial X} IV$$

where  $V$  is the volume of the principal ferromagnetic phase of magnetic moment  $I$ , and  $\frac{\partial H}{\partial X}$  is the rate of variation of  $H$  in the direction in which the force is measured. The magnetic moment  $I$  at high field strengths depends on the temperature and is only slightly dependent on strain; the distribution of phases does not enter into the equation. The measure-

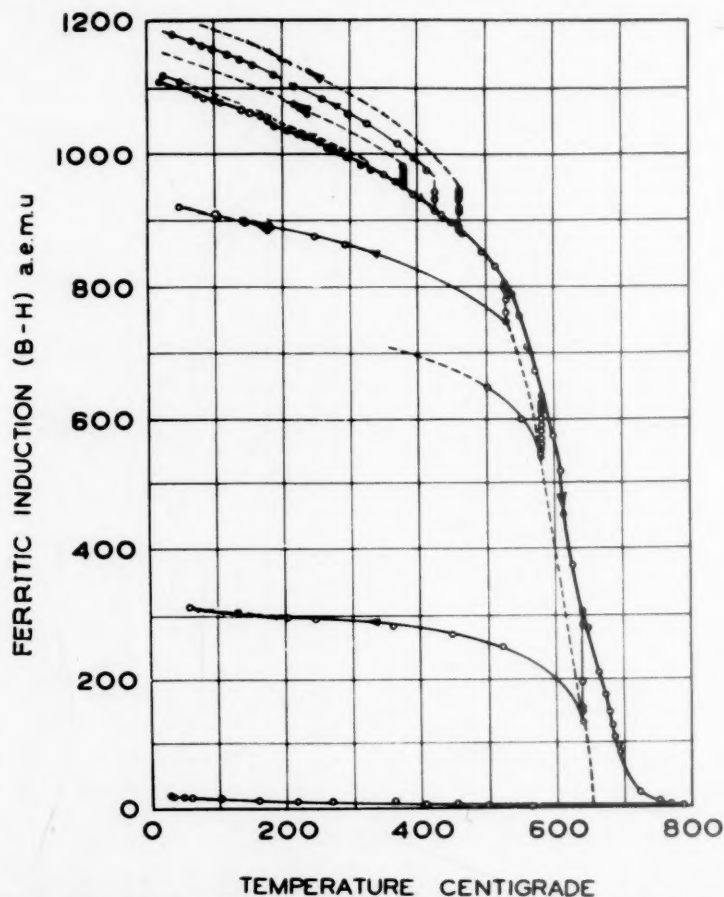


FIG. 3.—VARIATION OF FERRITIC INDUCTION DURING HEATING AND COOLING. SAME ALLOY AS IN FIG. 1.

Sample B. Annealed, quenched and cold-reduced by rolling, 50 per cent.

ments can be expressed in various ways. The average ferritic induction ( $B - H$ ) of the samples has been calculated for a field strength of 2000 absolute electromagnetic units, and was employed in the measurements. This average ferritic induction is equal to  $4\pi I$  times the percentage volume of the ferromagnetic component and is consequently proportional to the measured force divided by the volume of the specimen. When a small correction is made for stress relief, the percentage ferrite at any temperature is proportional to the corresponding induction. This

method of measuring the magnetic moment of a material has certain advantages over determining the magnetic induction of a quenched sample at room temperatures by usual methods: It is rapid and requires only small samples, and the various magnetic components of a given sample can be distinguished by their Curie points.

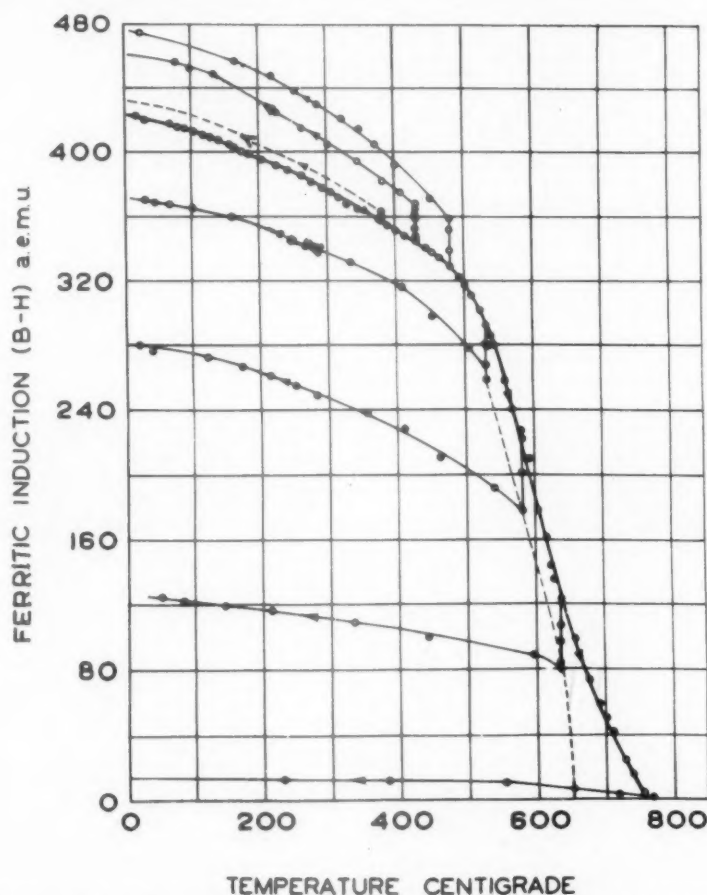


FIG. 4.—VARIATION OF FERRITIC INDUCTION DURING HEATING AND COOLING. SAME ALLOY AS IN FIG. 1.

Sample C. Annealed, quenched and cold-reduced by rolling, 24.5 per cent.

The alloy principally studied was in the form of strip of composition 18.13 per cent Cr, 8.95 per cent Ni, and 0.08 per cent C, the remainder being primarily iron. The strip was kindly furnished by R. H. Aborn, of the United States Steel Corporation Laboratories. It had been cold-rolled from different slab thicknesses of a forged and annealed austenitic ingot. All samples were of the same thickness but varied in the degree of cold reduction. In Fig. 1 the variation of the magnetic induction and the percentage volume of ferrite with cold-work are indicated. The calculation of the percentage volume of ferrite is based on the reasonable extrapolation of Aborn and Bain<sup>1</sup> that pure ferrite in 18-8 should have a magnetic induction of 13,000 a.e.m.u. when  $H$  equals 500 a.e.m.u. X-ray

measurements made by these authors as well as by us bear out the trend of the curve. It is necessary to point out, however, that the surface percentage of ferrite obtained by electron diffraction studies (to be published later) is in all cases much larger than the volume percentage. The samples suspended in the torsion balance were cut from the strip to the approximate size  $0.25 \times 0.25 \times 0.04$  in. These carefully cut

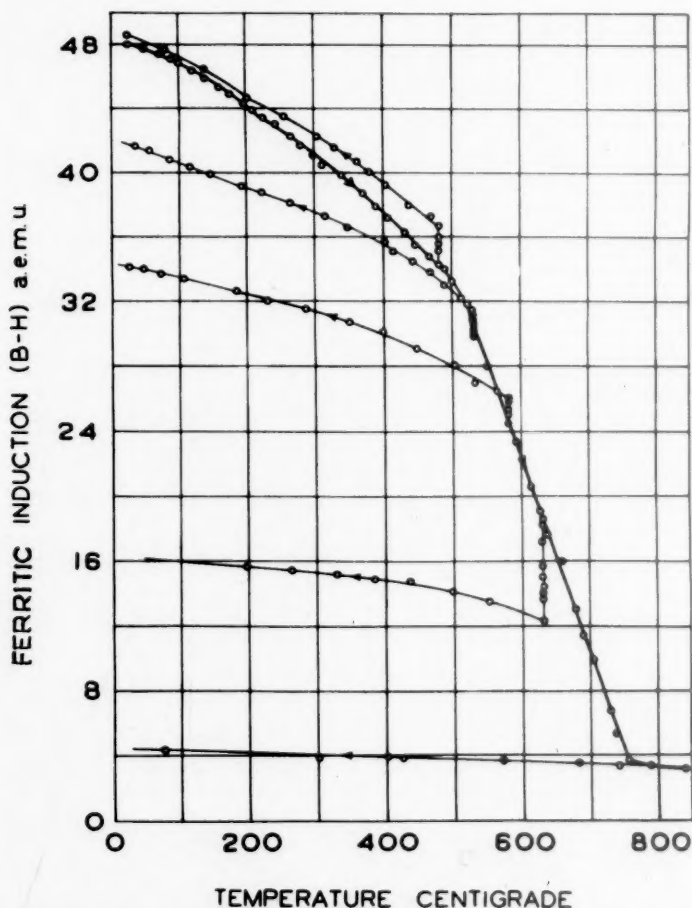


FIG. 5.—VARIATION OF FERRITIC INDUCTION DURING HEATING AND COOLING. SAME ALLOY AS IN FIG. 1.

Sample D. Annealed, quenched and cold-reduced by rolling, 9.1 per cent.

edges were then ground and pickled to remove enough of the freshly cold-worked material so that its contribution to the magnetic force was negligible.

The heavy-line curves of Figs. 2 to 7 represent the deviation of magnetic induction of the various samples of Fig. 1 when they are heated at a constant rate from  $20^{\circ}$  to  $900^{\circ}$  C. in 90 min. The vertical lines of Figs. 2 to 7 represent the magnetic behavior of samples held at a constant temperature for definite periods of time. These variations are plotted on a time scale in Figs. 8-13. The ferritic induction during cooling is also shown in Figs. 2 to 7 by the curves with arrows pointing toward

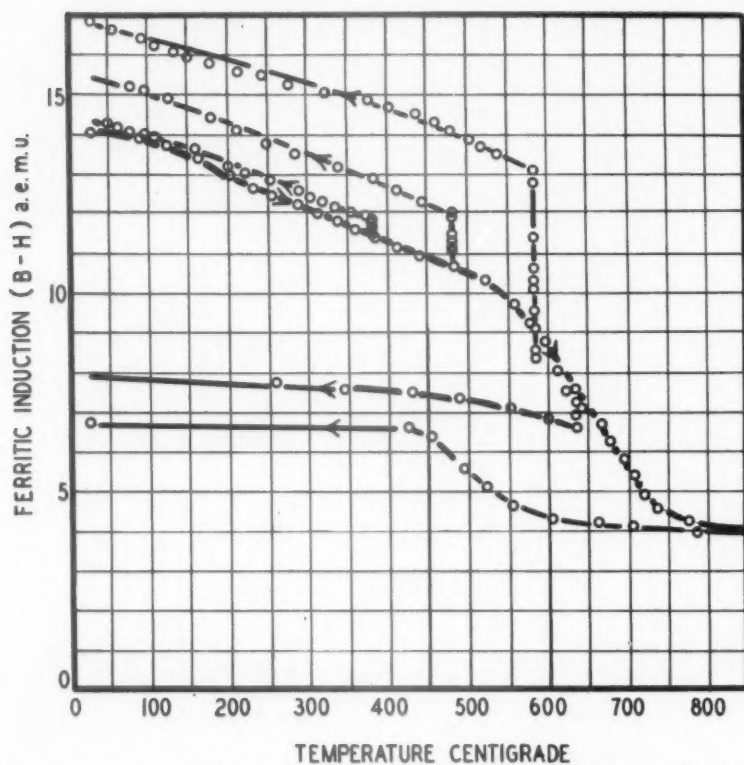


FIG. 6. Sample E. Annealed, quenched and cold-reduced by rolling, 2.4 per cent.

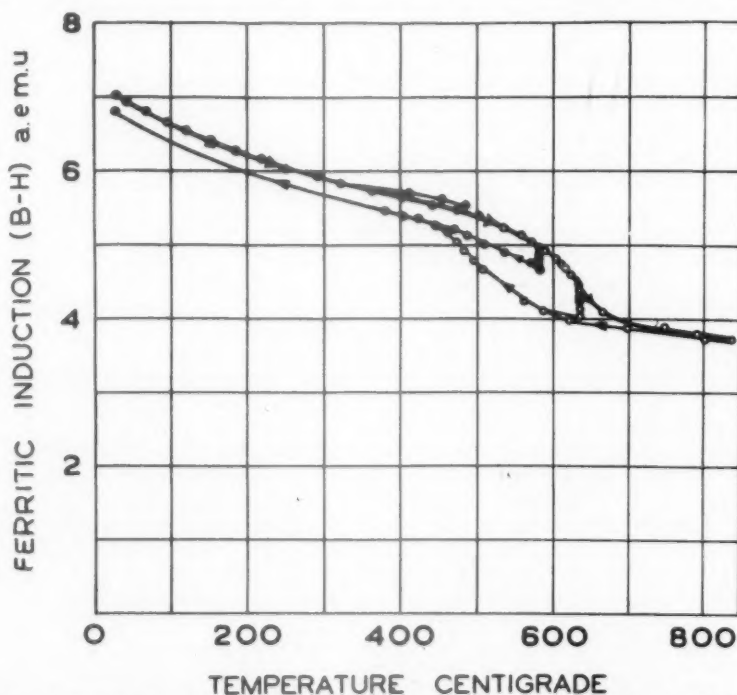


FIG. 7. Sample F. Annealed and carbide precipitated for 6 hr. at 600°C.

FIGS. 6 AND 7.—VARIATION OF FERRITIC INDUCTION DURING HEATING AND COOLING.  
SAME ALLOY AS IN FIG. 1.



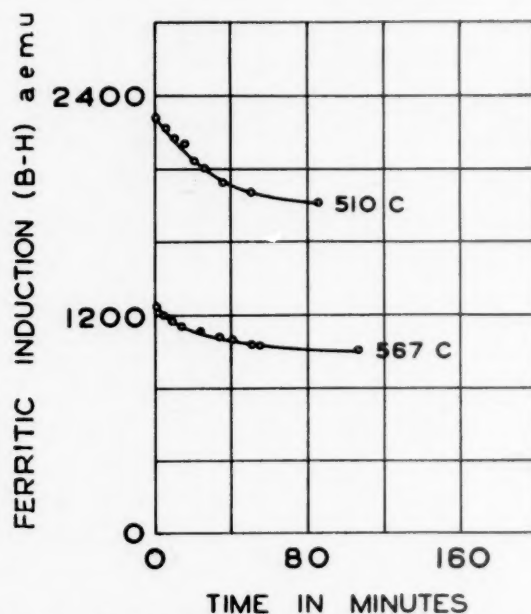


FIG. 8. Sample A. Annealed, quenched and cold-reduced by hammering, 83 per cent.

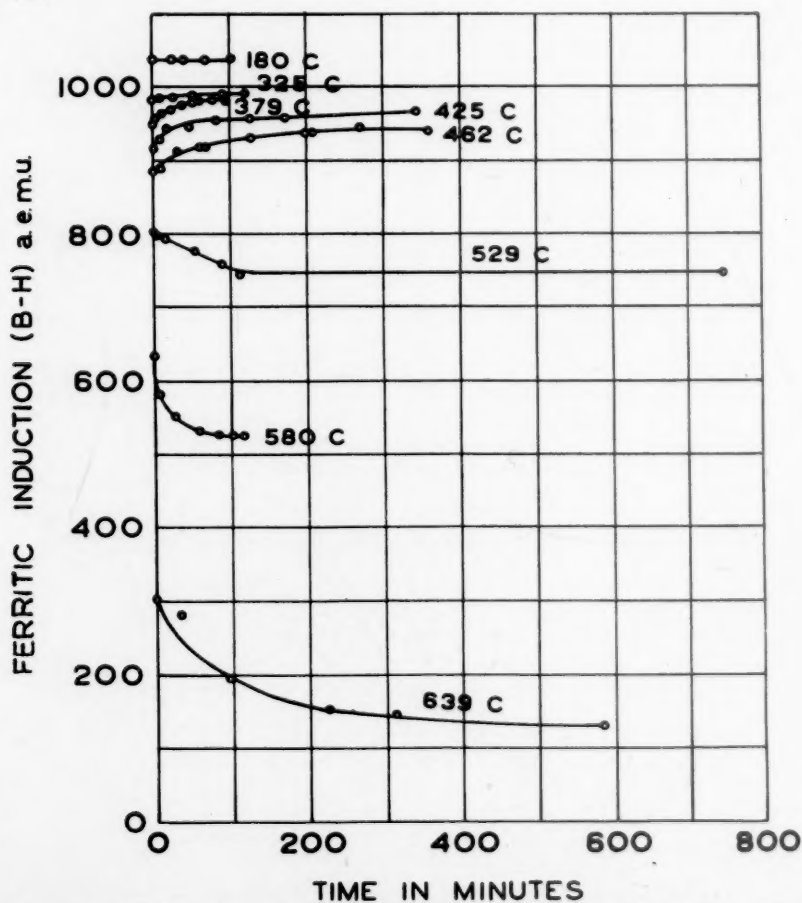


Fig. 9. Sample B. Annealed, quenched and cold-reduced by rolling, 50 per cent.  
FIGS. 8 AND 9.—VARIATION OF FERRITIC INDUCTION WITH TIME AT VARIOUS CONSTANT TEMPERATURES FOR SAMPLES OF FIGS. 2 TO 7.

decreasing temperature. These cooling curves also show the variation of magnetic moment of ferrite with temperature, since the percentage of ferrite does not change during cooling.

*Carbide as a Result of Cold Deformation and Low-temperature Annealing*

A reproducible discontinuity occurs in the curves of Figs. 2 to 7 near 200° C. Similar measurements made on 18-8 with a lower carbon

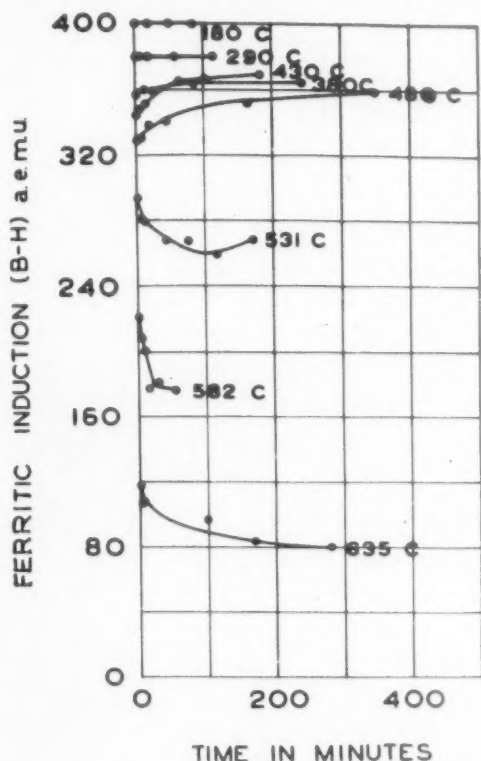


FIG. 10.

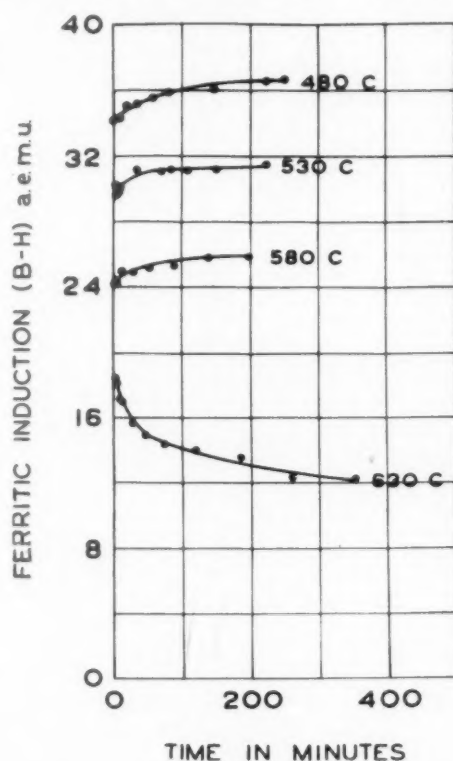


FIG. 11.

FIGS. 10 AND 11.—VARIATION OF FERRITIC INDUCTION WITH TIME AT VARIOUS CONSTANT TEMPERATURES FOR SAMPLES OF FIGS. 2 TO 7.

FIG. 10. Sample C. Annealed, quenched and cold-reduced by rolling, 24.5 per cent.

FIG. 11. Sample D. Annealed, quenched and cold-reduced by rolling, 9.1 per cent.

content (0.01 per cent) did not show a discontinuity at this temperature, but carbon steel and Armco iron containing more than 0.04 per cent C gave a similar discontinuity practically at 200° C. Consequently, the authors feel justified in ascribing the discontinuity to the presence of a carbide having the possible magnetic behavior of  $\text{Fe}_3\text{C}$  but containing some chromium in place of iron. Still doubtful of the experimental validity of the result, the experiments were repeated with different apparatus in the magnetic laboratory at Massachusetts Institute of Technology with the kind cooperation of Prof. F. Bitter and Prof. A. R. Kaufmann. Measurements at different field strengths up to

40,000 oersteds on the same 0.08 per cent C 18-8 and on a 0.09 per cent C 18-8 alloy indicated the presence of a Curie-point discontinuity in the curve at a temperature of 200° C. All further efforts by means of X-rays

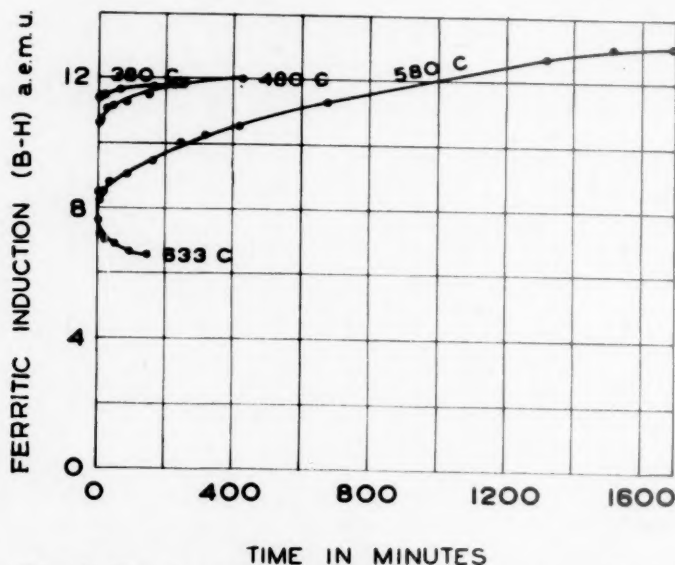


FIG. 12. Sample E. Annealed, quenched and cold-reduced by rolling, 2.4 per cent.

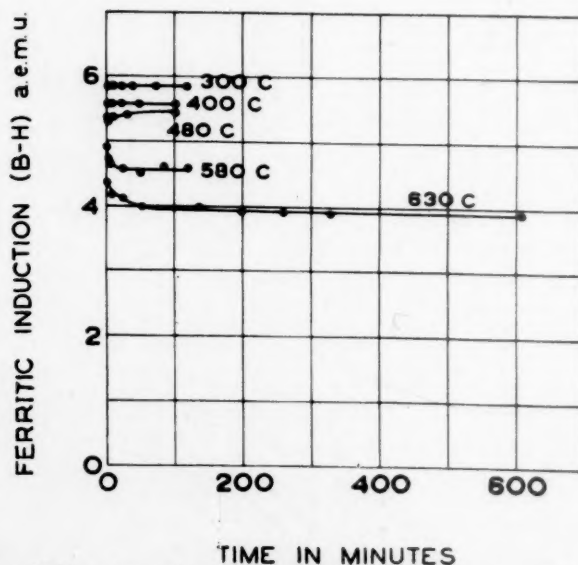


FIG. 13. Sample F. Annealed and carbide precipitated for 6 hr. at 600° C.

FIGS. 12 AND 13.—VARIATION OF FERRITIC INDUCTION WITH TIME AT VARIOUS CONSTANT TEMPERATURES FOR SAMPLES OF FIGS. 2 TO 7.

and electron diffraction to corroborate the presence of this phase proved fruitless, as was to be expected because of the small amount of the constituent and in all probability its fine subdivision.

In Fig. 14 a portion of Fig. 3 is plotted to a larger scale in order to show the inflection more clearly. Although the absolute magnitude of the ferritic induction has not been determined accurately, relative values are accurate to about 0.1 per cent, which justifies the use of the magnified scale. In Fig. 15 the percentage of carbon tentatively considered bound as iron carbide is plotted as a function of the magnetic induction or amount of ferrite present in the various samples. The calculation of the total volume of iron carbide present in each of the samples is based on an

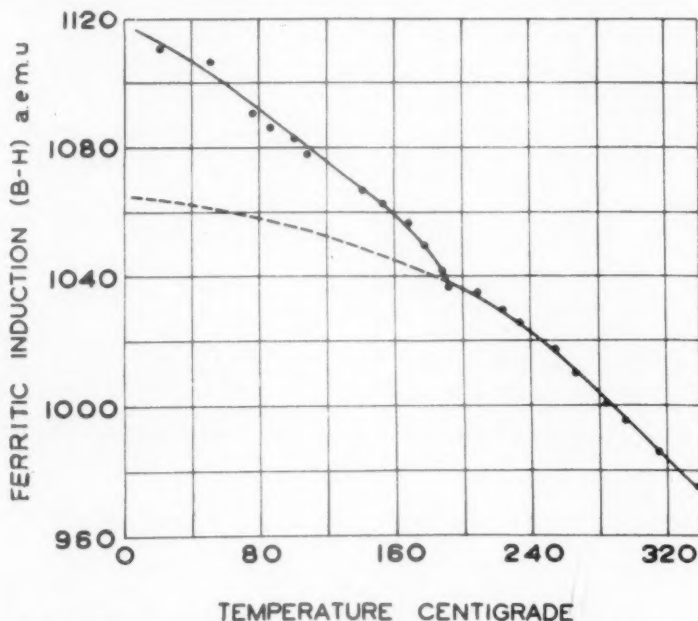


FIG. 14.—PORTION OF HEATING CURVE OF FIG. 3 PLOTTED TO A LARGE SCALE. Discontinuity near 200° C. shows presence of  $\text{Fe}_3\text{C}$ .

assumption the use of which is justifiable only as an approximation. By means of the curve for magnetic induction versus temperature of the steel containing 0.01 per cent carbon previously referred to, the magnetic induction of the ferrite can be extrapolated from above 200° C. to room temperature, as shown by the dotted curve in Fig. 14. Consequently, the difference between the curves represents the contribution of the iron carbide to the ferritic induction. This gives sufficient data to calculate  $B - H$  in a.e.m.u. The curve of Fig. 15 shows that the amount of this phase present is definitely dependent on the degree of cold reduction. Auxiliary experiments with 18-8 alloys of increasing carbon content (0.02 to 0.15 per cent) indicate a similar dependence on the carbon content.

From the standpoint of "aging," it is of interest to know whether the supposed cementite precipitate is effected by heat-treatment. The query is prompted by the divergent literature on carbides of varying chromium, iron and carbon content in the Fe-Cr-C system<sup>6</sup> as well as the fact that in making Curie-point determination the specimen is heated.

Preliminary results show that 24-hr. annealing at 150° C. does not affect the percentage composition of the cementite phase. Annealing at 250° C., however, results in a decrease of the cementite content of the alloy and the appearance of an additional magnetic phase whose Curie point is about 176° C. Annealing of cold-worked material at 345° C. for 24 hr. causes a disappearance of the 200° and the 176° Curie point and the appearance of another at 168° C. If the experiment is repeated on the same cold-worked stock annealed for 24 hr. at 395° C., all previous

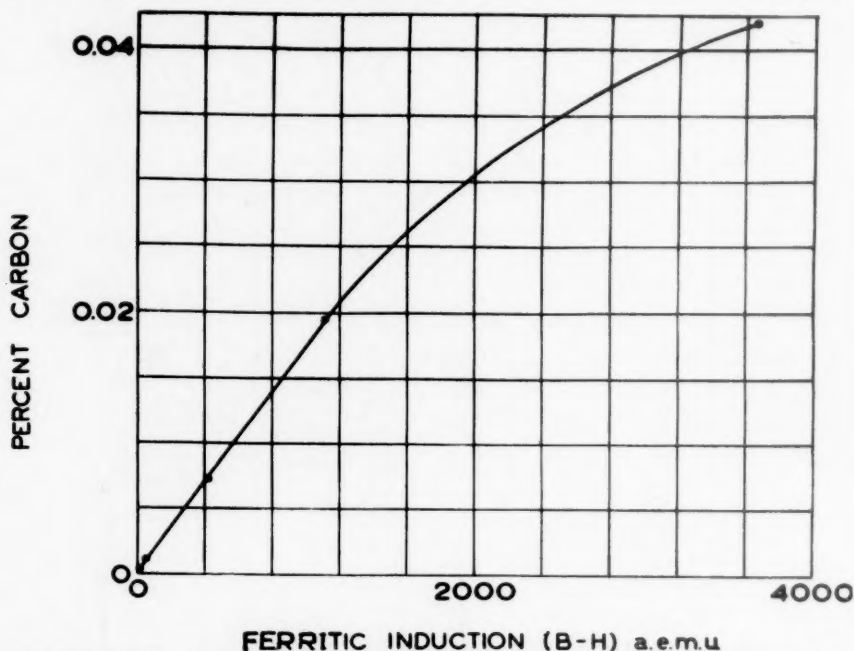


FIG. 15.—VARIATION OF PERCENTAGE OF IRON CARBIDE FORMED DURING ROLLING. Percentage of carbon as iron carbide  $\text{Fe}_3\text{C}$  depends on cold reduction, as does percentage ferrite and consequently ferritic induction. Therefore the percentage of carbon as iron carbide is plotted against the corresponding ferritic induction of the sample. The various points represent different amounts of cold reduction.

Curie points (except ferrite) disappear and a new one at 145° C. appears. Annealing at higher temperatures up to 800° C. before thermomagnetic measurements are made do not indicate the presence of any other magnetic phase except ferrite on samples that are thoroughly pickled. If not thoroughly pickled, Curie points of magnetic oxides can be determined.

Annealing experiments on cold-worked material are continued above 800° C. Although the experiments need to be carried much further, it can be stated that 24-hr. anneals at 1050° C. when quenched in water and pickled to thoroughly remove all oxide do not show the presence of a magnetic phase. If we anneal cold-worked material for shorter times (1 to 2 hr.), or employ cast stock that has not been cold-worked, a magnetic precipitate with a Curie point of 168° appears with or without the presence of some ferrite. Only the use of extremely fine wire suspensions in the torsion balance apparatus permits such observations as the above.



*High-temperature Carbide Precipitation and Ferrite Formation*

Samples of the cold-worked material, when annealed at 1050° C. and subsequently annealed for long periods at 600° to 800° C., exhibit the well-known phenomena of preferential grain-boundary precipitation of carbide, with the formation of ferrite a concomitant of this precipitation.<sup>1</sup> The ferrite exists primarily adjacent to the precipitate,<sup>1</sup> as can be shown by the precipitation of colloidal  $\alpha\text{Fe}_2\text{O}_3$ <sup>7,8</sup> when a magnetic field is applied

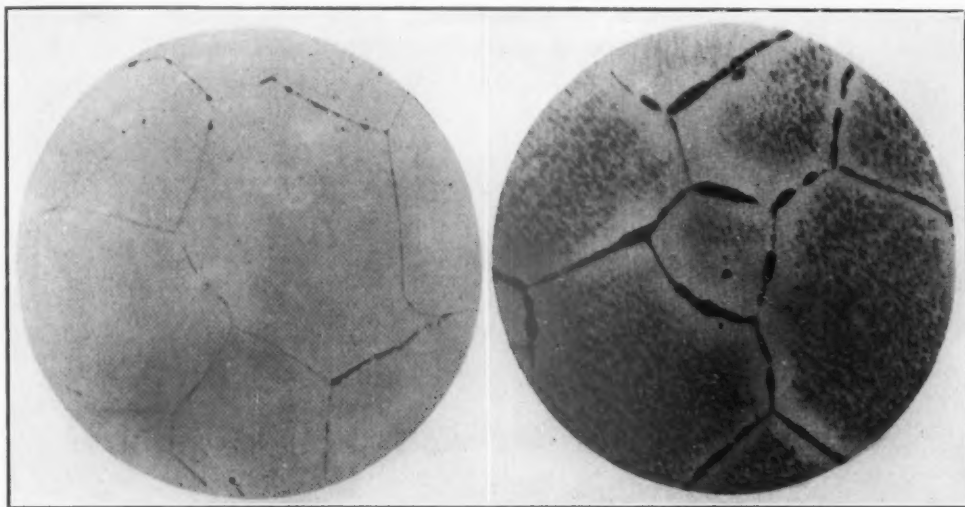


FIG. 16.—(a) POLISHED AND PICKLED 18-8 CARBIDE PRECIPITATED MATERIAL; (b) SAME MATERIAL BUT EXTREMELY WEAK SUSPENSION OF COLLOID WAS USED. ORIGINAL MAGNIFICATION 150; REDUCED APPROXIMATELY  $\frac{1}{4}$  IN REPRODUCTION.

Ferrite regions show dark, not owing to etching but to precipitation of colloidal iron oxide.

perpendicular to the specimen (Fig. 16). The ferrite thus formed has been considered to be of different composition because of chromium depletion.<sup>1</sup> Our magnetic results show, however, that the thermomagnetic curve for ferrite thus formed is the same as that for cold-worked ferrite. Data for a sample of cold-worked austenitic material (containing 0.02 per cent ferrite) are given in Figs. 7 and 13. When the sample is held for 10 hr. at 630° C., it loses its ferromagnetism entirely but regains magnetic characteristics on cooling; hence we presume to be dealing with a transformation rather than the precipitation of a material with a lower Curie point. On reheating the alloy to determine the Curie point of the ferrite present, we find it to be the same as in all cases studied. Thus the ferrite produced seems to be primarily due to local strains in the vicinity of the carbides. Such local strains should hardly be removed at temperatures below which carbon does not redissolve.

*Relief of Internal Strain*

Our measurements on cold-worked samples indicate that there is an increase of magnetic induction with time at constant temperature

between 325° and 480° C. This observation is in agreement with the work of Aborn and Bain<sup>1</sup> as well as of Akimow et al.<sup>3</sup> The increase of ferritic induction, however, does not necessarily indicate an increase in the percentage ferrite. Strains can be relieved at these temperatures, which would make the material magnetically softer and, therefore, would increase the ferritic induction. At saturation, however, the measured ferritic induction would be independent of strain. Consequently, to determine whether the increase of ferritic induction is due to an increase in the percentage ferrite or to the relief of internal strain, the magnetic measurements must be extrapolated to saturation; that is, to infinite field strength. At high field strength, most ferromagnetic materials approximately follow the relation

$$(B - H) = (B - H)_{\text{sat.}}(1 - a/H^2)$$

where  $(B - H)_{\text{sat.}}$  is the ferritic induction at saturation and should be independent of strain;  $a$  is a constant depending on the condition of the material including internal strain, and  $H$  is the field strength. This expression is supposed to hold when  $(B - H)$  is within 94 per cent of the value at saturation. The factor  $(B - H)_{\text{sat.}}$  depends only on the temperature and atomic arrangement; it should be independent of the presence of internal strain.

Fig. 17 shows that this relation is approximately satisfied in the 18-8 steels investigated. Measurements were made on the steel in three different conditions; namely: (1) unheated after cold-rolling, (2) heated in the range of temperature that causes an increase in magnetic induction, (3) heated to a higher temperature at which some ferrite still remains. Since the curve for the sample heated to 425° C. intersects that which was not heated after cold-rolling at  $1/H^2 = 0$ , both samples would appear to have the same percentage of ferrite, the difference in the measured ferritic induction being caused by the relief of strain. Because of the inaccuracies of extrapolation, however, some ferrite may possibly form during heating or because of low-temperature carbide precipitation, but we feel it is of insignificant amount. Heating to higher temperatures, however, results in a transformation of ferrite to austenite, since curve *C* of Fig. 17 of the sample heated to 640° C. does not intersect the other curves at  $1/H^2 = 0$ .

Our magnetic measurements do not offer a convenient means of measuring internal strain, for although ferritic induction is known to decrease with increase of strain, the rate of variation with strain is unknown. All that we can conclude from our data relative to internal strain is as follows: In 5 hr. at 440° C. a large portion of the strain that affects the magnetic hardness is removed, and a barely detectable amount is removed after heating for 24 hr. at 325° C.

*Ferrite-austenite Transformation*

In Figs. 2 to 13, the transformation of ferrite to austenite is indicated. Since this transformation starts at temperatures at which strain relief is simultaneously affecting the magnetic measurements, these measurements do not offer a reliable means of determining the lowest temperature at which transformation begins. By observing the changes in the slope of the heating curves, as well as by extrapolating from higher temperatures

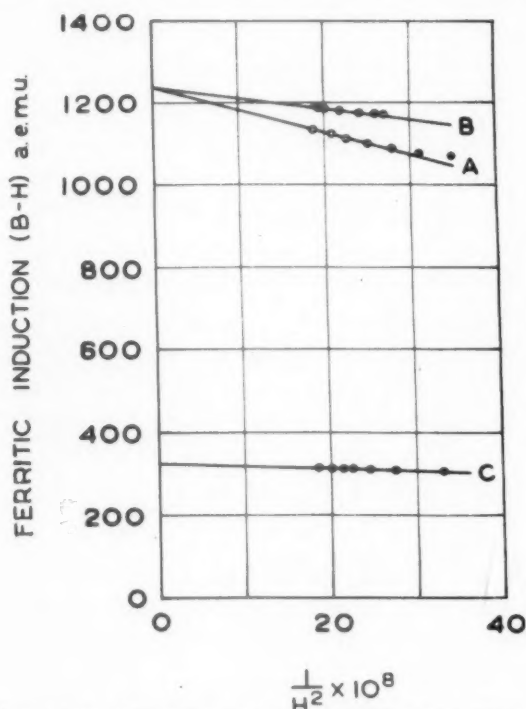


FIG. 17.—VARIATION OF FERRITIC INDUCTION WITH FIELD STRENGTH.

- A. Strained ferrite; no heat-treatment after cold-rolling.
- B. Strain partly removed by heating at 425° C.
- C. Strain removed by heating at 640° C.

the amount of ferrite transformed, the initiation of the  $\alpha$ - $\gamma$  transformation is seen to occur at about 440° C. for the more severely cold-worked samples and at a somewhat higher temperature for the less severely worked samples. This agrees with the work of Akimow et al. and approximately with Aborn and Bain. Long continued heating causes all the ferrite produced by cold-working to transform to austenite above 600° C., whereas rapid heating requires a higher temperature (about 750° C.).

It is interesting that the curves of Figs. 2 to 7 are essential duplicates of each other when considered as a percentage of the initial ferrite present, except for the effect of ferrite associated with high-temperature carbide precipitation in samples D and E (Figs. 5 and 6) and the austenite sample

with precipitated carbide (Fig. 7). Also, in the samples in which this precipitation of high-temperature carbide does not affect the magnetic measurements—namely, samples A, B and C Figs. 2 to 4—a relatively rapid decrease in ferrite occurs during about the first hour of heating, followed by a slower decrease above the temperature at which the relief of internal strain greatly affects the magnetic measurements (approximately 500° C.). This slower rate of decrease for longer heating times is shown in better fashion for quenched samples by the work of Aborn and Bain and by Akimow et al.

#### DISCUSSION AND CONCLUSION

In view of the checks and rechecks with the same and other apparatus on 18-8 from several ingots at different field strengths, we believe there is ample justification for describing the discontinuity near 200° C. in the thermomagnetic curves as a Curie point. That it is probably a carbide can be concluded from the results with low-carbon stainless steel. That it is  $\text{Fe}_3\text{C}$  can only be inferred from measurements on low-carbon steel and the known Curie point of cementite. To prove its crystallographic identity by X-ray or other methods would be difficult because of the fine dispersion and extremely small amount of material present.

The increase in amount of carbide present with increasing amounts of cold-work suggests that the work-hardening of 18-8 may not be due entirely to the formation of ferrite but also to the formation of carbide. The latter possibility sheds light on the work of Akimow and Friedmann,<sup>3</sup> who found that 18-8 rolled at various temperatures from 20° to 470° C. has the same hardness as cold-rolled material in spite of the fact that above 150° C. practically no ferrite is formed during working.

The magnetic measurements have also shown that the supposed<sup>1,3</sup> transformation of austenite to ferrite during heating between about 325° and 450° C. does not exist, and that the increase in magnetic induction observed by others is due to the relief of internal strain. Some strain relief apparently occurs as low as 325° C., but a temperature as high as 440° C. is required before a large portion of the strains that determine the magnetic hardness is removed.

The mechanism of ferrite formation due to high-temperature carbide precipitation may well be analogous to the formation of cold-worked ferrite. In this respect it is necessary to recall that our measurements do not indicate that ferrite formation is a concomitant of carbide precipitation at 750° C., but, rather, that the austenite adjacent to precipitated carbides transforms to ferrite only when the temperature of the sample is lowered below about 600° C. That there should be around the high-temperature carbide, when cooled to room temperatures, a high degree of strain, which would increase the velocity of transformation of the



boundary austenite, seems reasonable. This is in accord with the viewpoint of Kinzel<sup>3</sup> and Becket;<sup>4</sup> nevertheless, owing to the nonmagnetic nature of the high-temperature carbide, possibly because of its high chromium content, we cannot deny the possibility of some chromium depletion at the grain boundaries, as suggested by Aborn and Bain.<sup>1</sup> Although our measurements do not prove either viewpoint, they do indicate that the ferrite formed on cooling has similar magnetic characteristics to that of cold-worked ferrite.

The allotropic transformation in the alloy studied is complicated by a number of factors more or less interrelated. According to our measurements transformation of ferrite to austenite takes place over the temperature range of 440° C. to 650° C. In this range stresses are relieved and carbides rich in chromium are precipitated, and this precipitation may also cause the production of some new ferrite. The temperature at which the ferrite-austenite transformation occurs and the percentage of initial ferrite transformed seem independent of the total percentage of ferrite and consequently of the amount of previous cold-work. To present such a host of phenomena analytically or geometrically does not make for simplicity. For this reason we can best summarize our results by describing what takes place during the working and heating of the 18-8 alloy studied.

1. A cold reduction of 50 per cent produces about 9 per cent by volume of ferrite in an austenitic 18-8 alloy of 0.08 C content. A phase tentatively identified as iron carbide is formed during working.

2. Annealing above 250° C. causes this phase to disappear, but with the subsequent appearances at higher temperatures of new phases with successively lower Curie points. Such phases may also be considered as carbides of composition different from  $\text{Fe}_3\text{C}$ .

3. Annealing up to 440° C. releases some internal strains, thereby slightly increasing the magnetism of the alloy but not its major ferritic or austenitic content.

4. Annealing at higher temperatures initiates the  $\alpha$ - $\gamma$  transformation.

5. In the temperature range 600° to 800° C., nonmagnetic carbide precipitation occurs primarily in the grain boundaries of the material. Although ferrite completely transforms to austenite in this range, cooling of such an alloy with precipitated carbide below 600° C. results, nevertheless, in the formation of ferrite adjacent to the carbide precipitate. Above 800° C. carbides gradually redissolve and recrystallization commences.

6. Annealing cold-worked material in the temperature range 800° to 1100° C. for periods of 1 to 2 hr. and quenching permits the identification of a phase, probably a carbide, whose Curie point is 168° C. Annealing time of 24 hr. at 1050° C. give an austenitic material whose secondary constituents cannot be observed magnetically.



## SUMMARY

The phase transformations that occur in 18-8 stainless during cold-rolling and subsequent annealing were determined by magnetic-moment measurements at elevated temperatures. The precipitation, during cold-rolling, of a phase whose Curie point is  $200^{\circ} \pm 5^{\circ}$  C. has been tentatively identified as  $\text{Fe}_3\text{C}$ . The amount of this precipitated phase is a function of the degree of cold-work and of the carbon content of the material. No increase in this phase is found on annealing up to  $250^{\circ}$  C. for periods as long as 60 hr. Annealing for 24-hr. periods at increasing temperatures, however, causes the precipitation of successive phases possessing decreasing Curie-point temperatures. All indication of a Curie point or points disappears after 24-hr. annealing at  $700^{\circ}$  C. The increase of ferrite that others have observed in cold-worked material held at temperatures up to  $450^{\circ}$  appears from our measurements to be due primarily to the relief of internal strain rather than to phase transformation. The ferrite formed adjacent to carbides precipitated above  $600^{\circ}$  C. exhibits the same thermomagnetic properties as that produced by cold-work; ferrite does not form at the temperature of non-magnetic carbide precipitation, however, but is produced upon cooling to temperatures below  $600^{\circ}$  C. adjacent to such carbides.

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## DISCUSSION

(Gilbert Soler presiding)

F. R. MORRAL,\* Kokomo, Ind.—This paper is interesting because of the possibilities it suggests, and also because it shows the limitations of the method of magnetic analysis.

\* Research Metallurgist, Continental Steel Corporation.

The authors infer from their experiments that cementite with iron substituted by chromium is formed during working. This phase disappears on annealing at 250°C., but at higher temperatures new carbide phases appear, having a composition different from Fe<sub>3</sub>D. Apparently no effort has been made by the authors actually to determine these phases because they considered it would be difficult to prove their crystallographic identity by X-ray methods (p. 382).

Two papers by Professor Westgren are pertinent.<sup>9,10</sup> In stainless steels containing 13 per cent Cr and 0.1 to 0.4 per cent C, he separated and identified by means of X-ray powder photograms the face-centered cubic chromium carbide (Cr, Fe)<sub>23</sub>C<sub>6</sub>, with as much as 25 atomic per cent Fe. The parameter varied from 10.58 to 10.64 Å.

We have used frequently in the study of the Fe-W-C and Fe-Mo-C systems<sup>11</sup> the following method to separate the carbides: The alloy was dissolved anodically while the insoluble carbides were collected. The residue could be X-rayed, but gave diffuse photograms. The residue after a recrystallization treatment gave the same X-ray pattern with sharp lines, a pattern useful not only for accurate determinations of the lattice parameter, but also for intensity measurements to determine the actual crystal structure.

A. J. KLAPPERICH,\* Chicago, Ill.—The authors are to be complimented on the simple, sensitive and accurate apparatus for magnetic analysis and its application to the study of ferromagnetic materials.

Concerning the shift in the Curie point, for various time-temperature annealing ratios, I note that the Curie points were deducted from the "knee" of the ferritic induction-temperature curves. From work done here in the laboratory, we have been able to greatly alter the shape of a knee of a Curie curve; in fact, the whole curve can be changed, including the elimination of the "toe." This can be done by suitable choice of annealing atmospheres. Hence, I would like to raise a question as to the solidity of these points, inasmuch as they may be due to a changing knee structure rather than to an actual shift in the Curie point.

C. R. AUSTIN† and C. H. SAMANS,‡ State College, Pa.—The authors' work in magnetically analyzing the ferrite-austenite transformation is especially interesting to us because it looks as though it might be of great help in explaining some of the more puzzling features found in our work on the effect of preheat-treatment on the tensile deformation characteristics of an 18-8 stainless steel, which we hope to publish in the near future. All of our attention has been directed toward the range 600° to 800°C., where much of the authors' work seems to have been done.

Suppose a specimen had been annealed at 1066°C. and then reheated to a temperature, such as 750°C., at which appreciable carbide precipitation occurred; and that the material was then cooled to room temperature. The regions adjacent to the precipitate would presumably be changed to ferrite and would remain that way on cooling. Upon subsequent reheating at a relatively rapid rate to 600°, 700° or 800°C., might the retransformation of such ferrite to austenite take a relatively long time, say of the order of 700 or 800 hr. at 800°C., and proportionately longer at the lower temperatures? Some of our data seem to give indirect evidence that this occurs.

<sup>9</sup> A. Westgren, G. Phragmén and T. Negresco: *Jnl. Iron and Steel Inst.* (1928) **117**, 383-400.

<sup>10</sup> A. Westgren: *Jernkontorets Ann.* (1933) 501-512.

<sup>11</sup> F. R. Morral, G. Phragmén and A. Westgren: *Nature* (1933) 132, 61-62.

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From the authors' comments we should expect that the ferrite formed at temperatures of 600° to 800°C. would retransform to austenite in a relatively short time (10 hr. is mentioned for 630°C.) even if the alloy were not cooled, but the effect if it were cooled to room temperature and then reheated is the one about which we are curious.

H. HOLLOMON AND J. WULFF (authors' reply).—The authors appreciate Mr. Morral's suggestion concerning the possibility of using X-ray diffraction methods to determine the structure of the carbides found by magnetic analyses. This was initially tried for the different alloys employed, all containing less than 0.10 per cent C, without success, using the same technique as suggested. This is readily understandable in view of the fact that the percentage of carbon precipitated as carbide is 0.02 per cent for a 40 per cent cold reduction; furthermore, the fine subdivision of carbide prohibits the collection of a reasonably representative sample. Even after annealing treatment of the electrolytic residue sharp photograms were impossible. Should they have been obtained there would still be a question as to whether or not they had been altered by heat-treatment. By annealing the original cold-worked specimens at 600° to 750°C., it is possible to precipitate as carbide practically all the carbon in the alloys used and to separate it by electrolytic methods. However, this is a different carbide from that produced by cold-work. In this case, though, sufficient cubic carbide can be identified by X-ray methods. Some ferrite is always obtainable regardless of the degree of leaching employed. By going to higher carbon contents, as is shown by Westgren's work, one-phase structures are obtainable, yet these, we wish to point out again, have little if any relationship to the carbide precipitated as a result of cold-work.

We agree with Mr. Klapperich's suggestion that the shape of a Curie-curve knee may be altered by suitable choice of annealing atmosphere. To guard against this the low-temperature carbide Curie points were all determined on well pickled samples. Unpickled samples annealed above 300°C. show a Curie point at 120°C. in addition to those mentioned in the paper. This Curie point is due to oxide produced by annealing in air. After pickling, the new Curie curves showed no semblance of the oxide Curie point and practically no change in the knee of the curve. A study of surface changes produced by air annealing of 18-8 below temperatures of 250° to 300°C. convince us of the relative unimportance of annealing atmosphere provided, of course, that the magnetic measuring device used is of sufficient sensitivity.

The questions raised by Dr. Austin and Dr. Samans are of fundamental importance. According to their results it is possible to infer that the region next to intergranularly precipitated carbide is so radically depleted of chromium that annealing times of 700° to 800° hr. at 800°C. are not sufficient to homogenize this material, so that it has the physical properties of the grain interior. We have not carried out such long-time annealing experiments, yet from these as well as other unpublished measurements we can say that whenever the intergranular carbides are not redissolved (which undoubtedly they are not at 800°C.) some ferrite will always form adjacent to the carbides, but only on cooling due to local stresses. Thus the reheating of a sample in which carbides have been previously precipitated will cause adjacent ferrite to transform to austenite in a reasonable length of time at 800°C. Yet on cooling to temperature well below the Curie point of any possible residual ferrite, the austenite adjacent to the precipitated carbide begins to retransform to ferrite, not because of its different composition, but because of stresses developed around the carbides.

## The Nature of Passivity in Stainless Steels and Other Alloys, III—Time-potential Data for Cr-Ni and Cr-Ni-Mo Steels

By H. H. UHLIG\*

(Chicago Meeting, October 1939)

IN our study of the mechanism of and the prevention of corrosion in stainless steels, it was considered of fundamental importance to obtain knowledge of the surface structure of such alloys. If corrosion resistance is due to a self-healing oxide layer, which like a paint film protects the underlying metal, it would be obviously relevant were the effort made to make the film less permeable and more adherent; for example, the surface might be expected to respond to an anodizing process, which is found successful in increasing the film thickness and corrosion resistance of aluminum. However, if passivity and corrosion resistance of stainless steels are due to another cause, the attack of the problem would follow another path.

One of the most effective techniques for studying passivity and corrosion tendency is the measurement of the electrochemical potential. Not only can one determine by potential measurements whether a metal is active or passive, but also one can determine the degree of passivity and rate of transformation of passivity with time. Chemical media that build up or destroy passivity when in contact with the steel can also be classified by potential measurements. Something can be learned, too, of the effect of alloy additions such as molybdenum to 18-8, known to decrease corrosion of the alloy in chloride solutions.

A study of alloys in previous investigations has sometimes included data on the electrochemical potentials. Tammann and Sotter<sup>1</sup> measured the electrochemical potentials of alloys of iron-molybdenum and iron-chromium and reported the critical concentration of molybdenum or chromium at which passivity initiates. Strauss<sup>2</sup> made similar measurements for the iron-chromium system. The electrochemical potential<sup>3</sup> has also been used to indicate carbide precipitated 18-8. In 18-8, heat-treated to precipitate carbide, active metal exists at the region of the grain boundaries, contrasted with passive metal within the grains, the active metal accounting for a resultant active potential. Several

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Manuscript received at the office of the Institute April 27, 1939. Issued in T.P. 1121 in METALS TECHNOLOGY, October 1939.

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<sup>1</sup> References are at the end of the paper.



investigators<sup>4-9</sup> have measured potentials of metals as a function of time. In some measurements, an indication was obtained of whether the corrosion process was anodically or cathodically controlled. In others, when the electrodes changed from a steady initial potential to one that was more active, either spontaneously or by scratching, it was interpreted as disruption of a supposed protective film covering the electrode.

In this paper, results of potential measurements of some stainless steels as a function of time are presented with special reference to the effect of molybdenum added to 18-8. A study of the mechanism of the

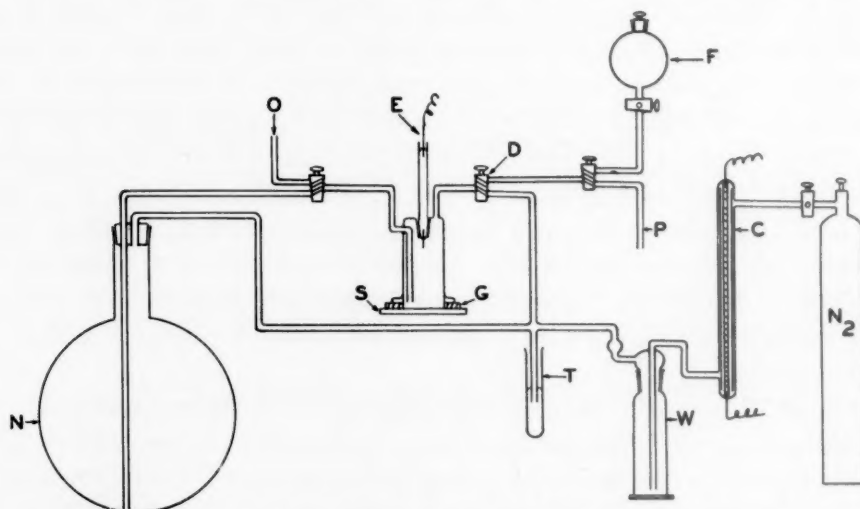


FIG. 1.—ARRANGEMENT OF CELL FOR POTENTIAL MEASUREMENTS.

action of molybdenum in 18-8 is of interest because molybdenum contributes considerably to the resistance of the alloy to attack by chlorides. The measurements were made in air-saturated and in oxygen-free sodium chloride solutions. Preliminary information was also obtained on the types of substances that destroy passivity of the alloys, something about the rate at which they do so and the time of complete recovery to the passive state. Finally, a discussion of the possible mechanism of action in each case has led to a plausible conception of the surface behavior of passive metals and alloys.

#### EXPERIMENTAL PROCEDURE

The potentials were measured using a type K potentiometer and a vacuum-tube null-point galvanometer. The cell containing the steel electrode and reference electrode, together with some auxilliary apparatus, but not drawn to scale, is shown in Fig. 1. All the apparatus except the nitrogen tank and nitrogen-purification tube *C* was kept within an air thermostat maintained at  $25^{\circ}\text{C.} \pm 0.1^{\circ}$ . The cell measured 2 by  $\frac{3}{4}$  in. The potentials were always measured in 4 per cent NaCl (4 grams



NaCl to 96 grams water) so that an Ag-AgCl electrode E was convenient for maintaining a constant half cell potential with respect to this solution. The Ag-AgCl electrode was prepared according to a method proposed by Brown.<sup>10</sup> It fitted into a socket of the cell by means of a ground-glass joint lubricated with stopcock grease. This electrode was checked frequently against other electrodes of the same kind and also against a calomel cell. The stainless-steel specimen *S* forming the other half of the cell was clamped to provide a gastight seal by means of rubber gasket *G*. The rubber gasket was also coated with stopcock grease. The nitrogen used to circulate the sodium chloride solution was first freed of traces of oxygen by passing over a 21-in. length of rolled copper screen *C* heated electrically by a Nichrome resistance coil passing through the center. The nitrogen then passed through a wash bottle *W* containing 4 per cent NaCl and connected either with the container *N* (5 liters) for oxygen-free 4 per cent NaCl or the cell at inlet *D*. *T* is a test tube filled partly with mercury to act as a pressure release. The sodium chloride in *N* was deoxygenated by bubbling through it a gas stream of nitrogen (deoxygenated at *C* and humidified at *W*) at a slow rate for 7 hr. The Winkler test for dissolved oxygen<sup>11</sup> indicated that oxygen in this manner was removed from 5 liters of solution at the end of approximately 4½ hr. The test for dissolved oxygen was made periodically during a series of potential measurements, to ensure that for all solutions used the presence of oxygen remained negative.

The steel specimens were first abraded with emery paper, using progressively finer grades down to 00 metallographic paper, then cleaned in ether and acetone and finally in distilled boiling benzene. The analyses of the rolled sheet steels used are given in Table 1. Minor constituents are not listed but appear in amounts normal to such steels.

TABLE 1.—*Analyses of Steels*

Constituent	Chrome-nickel Steel, Per Cent	Chrome-nickel-molybdenum Steel, Per Cent	Chrome-nickel-molybdenum Steel of Varying Percentages of Molybdenum
Cr	17.25	20.92	19.46
Ni	9.37	9.75	9.37
C	0.05	0.06	0.05
Mo		2.90	

The procedure followed in the majority of measurements was to open the cell to nitrogen gas for a few minutes to flush out air, then to fill the cell with oxygen-free 4 per cent NaCl. The potential taken at this time corresponded to that of a noble alloy, was usually not constant and was reproducible only within a range of about 0.15 volts. The

trend of potential was in most cases toward partial activity at a uniformly slow rate. This potential served mostly to check the various features of the cell and electrical circuits and to ensure that the steel specimen was in its normal state of passivity. Recently pickled samples are found, for example, to remain active or partly active for many hours afterward, and were not used for any of the potential determinations. The sodium chloride was then forced out of the cell by nitrogen. Hydrochloric acid or any other solution could then be admitted to the cell from *F*. Because this solution would ordinarily injure the reference electrode were it to come in contact with it, the cell was designed so that the solution filled the cell only to a depth of  $\frac{1}{2}$  cm., determined by the position of the inner glass tube above the specimen. 6N HCl was allowed to remain in contact with the alloy specimen for 10 min. to destroy passivity, or, its equivalent, to produce activity. It was determined by experiment that the activation process is complete in somewhat less than 10 min. and that by allowing the acid to remain for this time the potentials were satisfactorily reproducible. Oxygen-free sodium chloride was then used to wash out the hydrochloric acid. This entered the cell from *N*. When all the acid was washed out, as determined by a litmus test at outlet *P*, the potential of the steel was again measured. The potential of 18-8 after this treatment was more active by about 0.5 volt, and allowing a few minutes contact with oxygen-free sodium chloride was reproducible at  $0.51 \pm 0.01$  volt. Several further treatments of the specimen with acid no longer changed this equilibrium potential.

### RESULTS

The 18-8 specimens subjected to a 10-min. treatment with 6N HCl and then remaining in contact with oxygen-free sodium chloride showed a constant potential whether or not the sodium chloride solution was renewed several times during a series of measurements. This indicated, among other things, that no oxygen was entering the cell from any source. The potential over several days remained constant, or the steel became slightly more active represented by 0.01 or 0.02 volts. The similar alloy containing 3 per cent Mo under identical conditions showed an approximately similar potential after treatment with hydrochloric acid. The outstanding distinguishing difference, however, was that the molybdenum alloy at first rapidly, later more slowly, became noble with time in the *complete absence of dissolved oxygen*. In 10 to 15 hr., the molybdenum-bearing chrome-nickel steel specimens completely recovered passivity in oxygen-free sodium chloride. The results are shown in Fig. 2. These and following potentials were measured with reference to the Ag-AgCl electrode. To reduce the potentials to the hydrogen scale, 0.24 volts should be subtracted from all the values of potentials as given. The initial potentials of 18-8 and the corresponding molyb-

denum alloys in oxygen-free sodium chloride are shown to exhibit values in the noble ranges, not very reproducible under the best of conditions. The values of the potential on first bringing sodium chloride solution into contact with the specimens are usually more noble than the values after several minutes. The alloys containing molybdenum were in general more noble initially than the 18-8's. From 0 to 0.15 volts as measured vs. Ag-AgCl, or from  $-0.24$  to  $-0.09$  volts on the hydrogen scale represents the extreme ranges of values observed. The active potential for 18-8 was more reproducible than the initial potential, but the value of the active potential for the similar alloy containing 3 per cent Mo decreased rapidly immediately after acid treatment. The value obtained as soon as possible after washing out the acid from the cell was higher than the 18-8 value, and in some instances was as high as 0.60 volt. The value within a few minutes dropped some centivolts and later decreased more slowly until it finally reached its original noble value or became even more noble. The 18-8 active potential in oxygen-free sodium chloride remains approximately constant, so far as we know, indefinitely. The longest time of measurement on the same specimen was about four days.

The interesting behavior of these two steels prompted similar experiments using air-saturated 4 per cent NaCl, and air-saturated, as well as oxygen-free distilled water. The potentials reported as before were all measured in 4 per cent NaCl. This procedure was possible in view of the fact that sodium chloride was in contact with the alloy only a matter of minutes and any changes in passivity of the alloy during measurements were negligible. The results are included in Fig. 2. It is interesting that 18-8 in air-saturated sodium chloride does not regain complete passivity after it has been activated by acid. The potential levels off at about 0.3 volt and varies in this neighborhood as long as the measurements are continued. If the alloy is initially noble, however, and placed in contact with air-saturated sodium chloride, the potential usually tends in the opposite more noble direction rather than the active direction, as shown in the plot of results in Fig. 3. This is also true for the 18-8 alloy that has regained nobility by contact with oxygen-free distilled water, discussed below.

The data of Fig. 2 show, furthermore, that the alloy containing molybdenum very rapidly recovers passivity in air-saturated sodium chloride. This, as stated previously, is not true for 18-8. In oxygen-saturated water, however, 18-8 rapidly recovers passivity, so that apparently the presence or absence of electrolyte accounts for the rate at which the alloys transform, the electrolyte tending to slow up or inhibit transformation from the active to the passive state. In oxygen-free water, 18-8 slowly recovers passivity much as does the molybdenum alloy in oxygen-free sodium chloride solution. The results consistently point to the ability of molybdenum to stabilize the passive state.

It should be noted that values of potentials plotted in Fig. 2 are for more than single specimens of steel for any one series of measurements.

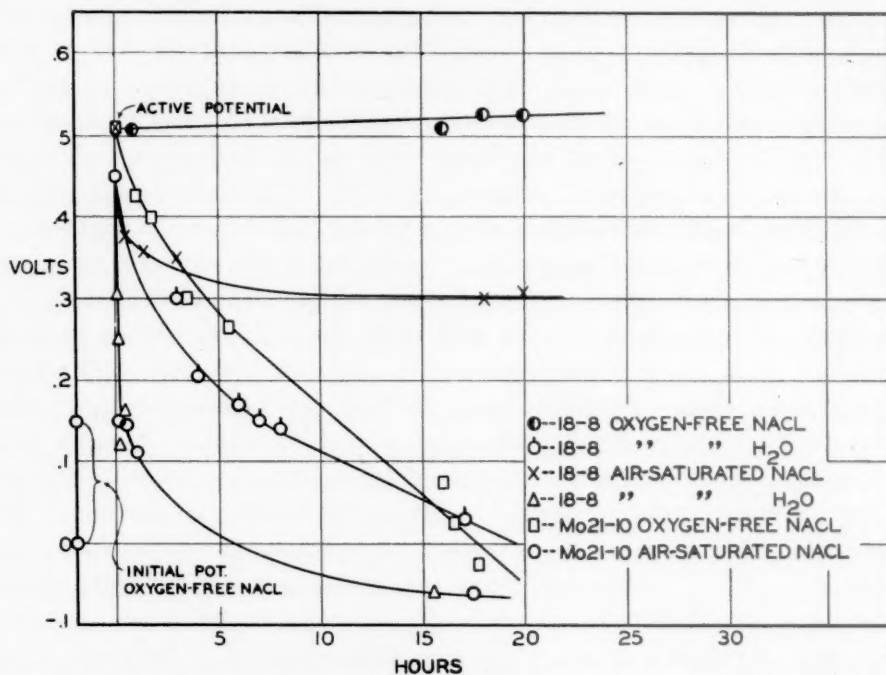


FIG. 2.—TIME-POTENTIAL DATA FOR 18-8 AND SIMILAR ALLOY CONTAINING 3 PER CENT MOLYBDENUM.

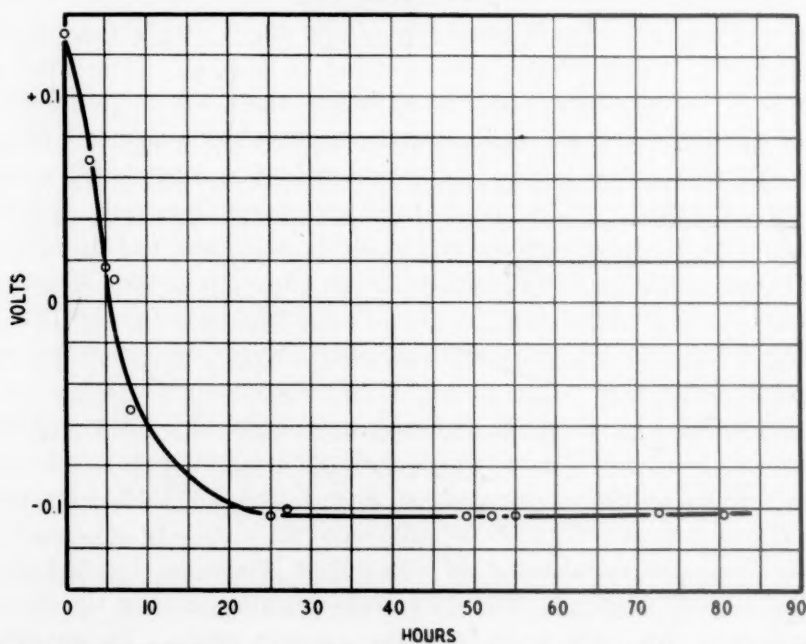


FIG. 3.—TIME-POTENTIAL DATA FOR 18-8 IN AIR-SATURATED 4 PER CENT NaCl.

For any group of samples of similar steels, the trend of potential is always in the same direction and leads to the same conclusions. Only for the



stainless steels initially noble in aerated sodium chloride does the potential sometimes become more active, sometimes more noble.

### *Molybdenum in 19-9*

A study of the effect of varying additions of molybdenum to 19-9 on the potential-time curves was made possible by samples of steel castings prepared by Mr. Lutz, of the Boston Navy Yard, specimens of which were kindly placed at our disposal. The analysis of the master alloy is included in Table 1. The measurements were made on sections

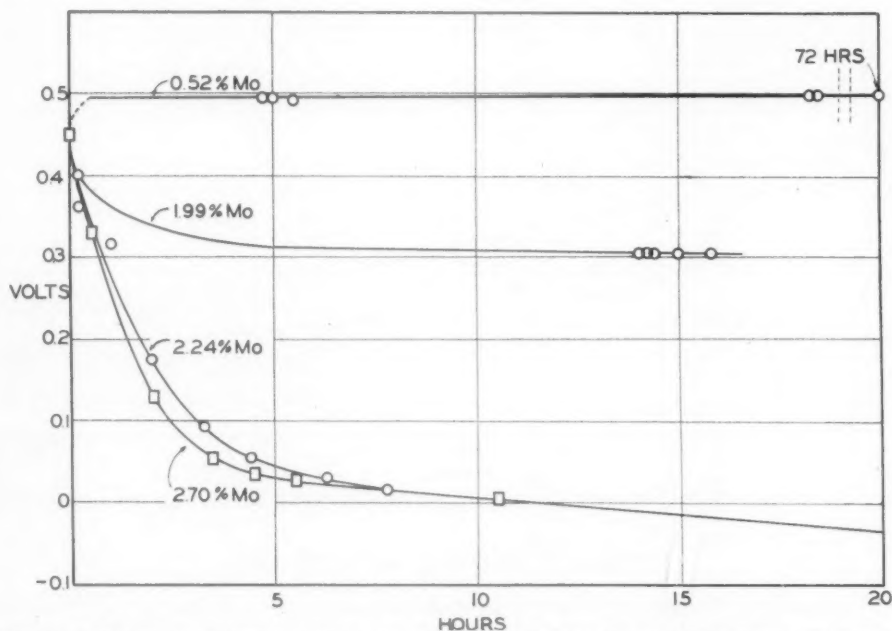


FIG. 4.—TIME-POTENTIAL DATA FOR 19-9 WITH VARIABLE MOLYBDENUM CONTENT.

of castings prepared as were the previous samples. The results are plotted in Figs. 4 and 5 for the steels in oxygen-free 4 per cent NaCl with determined percentages of molybdenum indicated on the curve for each alloy. It is evident that 0.5 per cent Mo has no effect in ennobling the alloy in oxygen-free sodium chloride, nor does 1.99 per cent show any marked effect. At 2.24 per cent Mo, however, the ennobling effect of molybdenum is definitely apparent. Above this percentage there is no obvious correlation of the percentage addition of molybdenum and the time curves. The spread of the data is somewhat larger than would ordinarily be expected. To account for this, the possibility arises of the effect of inhomogeneities, voids and inclusions in the specimen faces, much more evident in these castings than in the cold-rolled specimens used for previous measurements. The surface condition may have been the cause noted in some specimens of a lapse of passivity after 20 hr. in specimens that had completely regained passivity at the end of 5 or



10 hr. The alloys that showed this tendency became 0.2 to 0.3 volt more active after having already transformed spontaneously from the active to the passive state. This effect was not always reproducible for any one specimen, and possibly depended on a critical balance of anodic and cathodic areas on the specimen surface.

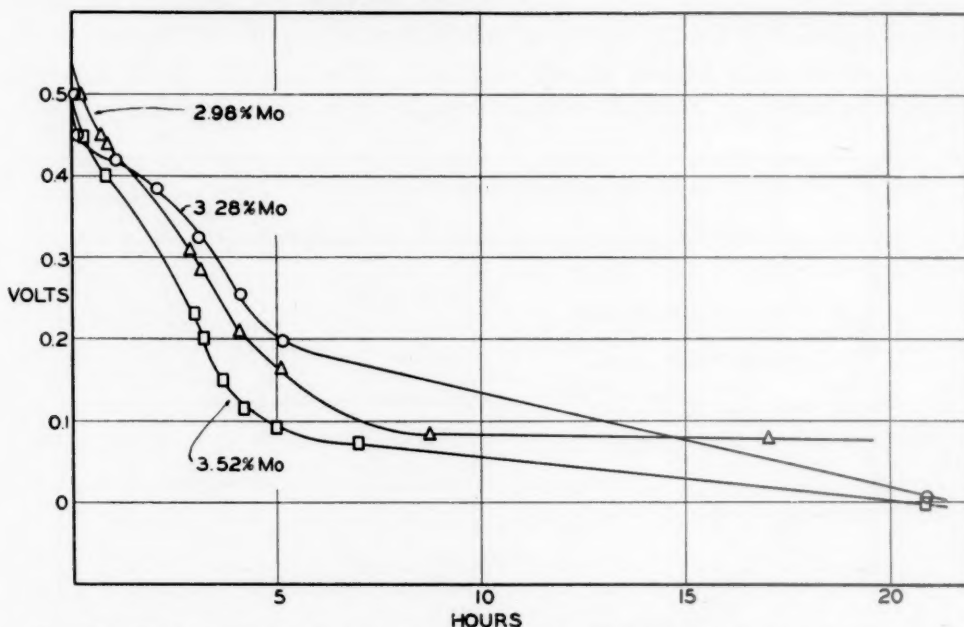


FIG. 5.—TIME-POTENTIAL DATA FOR 19-9 WITH VARIABLE MOLYBDENUM CONTENT. ]

#### *Chemical Passivators and Activators*

The potential apparatus used was convenient for obtaining further information on the ability of certain chemical media to build up or destroy passivity. The various solutions were admitted to the cell, as was 6N HCl, and definite time (10 min.) of contact with the steel was allowed. The cell was then flushed with oxygen-free 4 per cent NaCl and the potential recorded immediately, again 10 min. later and a third time 20 min. after flushing. Usually the potential decreased (more noble) when the steel was in contact with oxygen-free sodium chloride for some minutes. The results are tabulated in Table 2. It was found, for example that 6N HNO<sub>3</sub>, as expected, left the steel passive. A second 10-min. treatment, not shown in Table 1, made the steel more passive and dropped the potential in oxygen-free sodium chloride to -0.04 volts. Ferrous chloride, a corrosion product of 18-8, on the other hand, destroys passivity. This ability of ferrous chloride, in common with other acid chlorides, to destroy passivity is intimately linked with the action of pit growth in passive alloys, and especially takes part in the mechanism of the elongated pit in the direction of gravity observed for many specimens of 18-8 immersed for some months in sea water.

This theory has already been discussed in brief<sup>12</sup> and will be published in detail separately. Other acids besides HCl break down passivity but this is not a function of pH alone, but rather of pH and the nature of the negative-ion constituent. This is particularly brought out in comparing the action of 0.05 molal potassium acid phthalate with that of the mineral acids of equivalent pH. Potassium acid phthalate is a nonoxidizing acid whose action is neither passivating nor activating, the noble potential listed in Table 1 representing the initial potential of the steel as well as the potential after contact with the phthalate

TABLE 2.—*Potentials of 18-8 Stainless Steel in Oxygen-free 4 Per Cent NaCl versus Ag-AgCl after Treatment with Various Solutions*

Solution	pH	Potential Immediately after 10-min. Treatment, Volts	Potential 10 Min. Later, Volts	Potential 20 Min. Later, Volts
6N H <sub>2</sub> SO <sub>4</sub> .....	1.4	0.52		
6N HNO <sub>3</sub> .....		0.10		
FeCl <sub>2</sub> (saturated).....		0.42		
20 per cent NaOH.....		0.41		
20 per cent NaOH + KMnO <sub>4</sub> ....		-0.12		
0.05 M potassium acid phthalate..	3.98	0.04		
9N HCl.....	1.03 2.02 3.07 4.09	0.54	0.54	0.54
6N HCl.....		0.53	0.52	0.52
3N HCl.....		0.54	0.54	0.55
0.1N HCl.....		0.68	0.67	0.65
0.01N HCl.....		0.59	0.60	0.58
0.001N HCl.....		0.44	0.38	0.35
0.0001N HCl.....		0.13	0.21	0.20
CH <sub>3</sub> COOH.....	1.96	0.53	0.51	0.47
CH <sub>3</sub> COOH.....	2.98	0.63	0.61	0.55
CH <sub>3</sub> COOH.....	4.02	0.58	0.53	0.51

solution. Surprising is the result that sodium hydroxide, normally supposed to build a protective film on ferrous alloys, breaks down passivity rather than builds it up. The similar caustic solution, however, passivates 18-8 if a small amount of oxidizing agent like KMnO<sub>4</sub> is added to the solution. The chromium-nickel-molybdenum steel behaves similarly.

The effect of acid concentration on potentials of acid-treated specimens is fairly complex. These data as listed are only preliminary; more will be necessary to afford a complete explanation. It appears that negative-ion constituent again plays a role and possibly in addition oxygen solubility in acids, as one compares the potentials of steels subjected to hydrochloric acid at a given pH with the potential of the

same steel subjected to acetic acid at an equivalent pH. Acetic acid, for example, at a pH of 2.98 produces a potential of 0.63 volts, whereas hydrochloric acid at a similar pH of 3.07 produces a potential of 0.44 volts. Furthermore, acids of intermediate concentration apparently produce a more active surface than do the more concentrated acids. Steels activated by acetic acid, it was observed, unlike steels activated in hydrochloric acid tended to transform slowly in oxygen-free sodium chloride to the passive state over a period of 15 to 20 hours.

### *Nickel, Iron and Chromium*

Although extensive data were not obtained, it was found that pure metal constituents of 18-8 behaved in a manner analogous to that of the alloy (Table 3). Nickel and chromium are passive elements in the

TABLE 3.—*Potentials of Pure Metals in Oxygen-free 4 Per Cent NaCl versus Ag-AgCl before and after Treatment with 6N HCl*

Metal	Initial Potential in Oxygen-free 4 Per Cent NaCl, Volts	Potential Immediately after Treatment in 6N HCl, Volts	Length of Time of Acid Treatment, Min.	Potential 10 Min. Later, Volts	Potential after Exposure to Air, Volts
Nickel.....	0.40	0.47	10	0.47	0.22
Iron (cold-rolled mild steel).....	0.73	0.75	5	0.74	0.70
Chromium, plated on 18-8.....	0.60	0.85	3	0.60	0.50
Chromium, Thermite reduced.....					0.0-0.3
Platinum.....	-0.32	-0.34	10		-0.31

normal state and exhibit, as does stainless steel, active as well as passive potentials. The potential of iron similar to nickel and chromium is affected by hydrochloric acid treatment, although the change produced is not as pronounced. Chromium in oxygen-free sodium chloride appears to drift at a pronounced rate toward a noble potential after acid treatment, whereas the effect was not observed in the same degree for iron or nickel. In this respect chromium is like 18-8 containing 3 per cent Mo. Because of pronounced evolution of hydrogen, iron and chromium were treated for a shorter time with hydrochloric acid than was nickel or platinum. A longer treatment would not have altered the active potentials. The potentials of iron and nickel were measured for the pure-metal rolled sheet. Chromium specimens were obtained by heavy-electroplating on stainless steel. Freshly plated chromium was found to be active, but after air exposure for several hours became less active. Thermite-reduced chromium was found to be noble. This is in agreement with previous observations of other investigators.<sup>13</sup> Platinum showed no large fluctuations in potential regardless of surface treatment.

The potentials were never seemingly equilibrium values, but fluctuated a few centivolts on either side of a mean value. Iron, chromium, and nickel potentials in sodium chloride fluctuated less, however, and the effect of acid treatment on these metals was always unmistakable.

### DISCUSSION OF RESULTS

It is apparent that the potential measurements listed in the foregoing pages are subject to some variation in interpretation, yet some conclusions, which are immediately obvious, can be made regardless of interpretation. These are:

1. Stainless steel of the 18-8 variety and that containing in addition 3 per cent Mo can regain passivity in aqueous media in the complete absence of dissolved oxygen. Any hypothesized film on stainless steel as cause of passivity cannot, therefore, be an oxygen film.

2. Although 20 per cent NaOH destroys passivity, the same solution containing  $\text{KMnO}_4$  passivates stainless steels. If a metal oxide or hydroxide passive film be hypothesized for stainless steels, the oxide or hydroxide must be, corresponding to the hypothesis, soluble in caustic solutions, but not soluble in the same solution containing  $\text{KMnO}_4$ . Actually iron and nickel hydroxides and oxides are insoluble in cold 20 per cent NaOH. Chromic hydroxide is soluble in NaOH and with  $\text{KMnO}_4$  forms a precipitate, probably hydrated  $\text{MnO}_2$ , which however is soluble in nitric acid and hence does not fit the requirements of the supposed passive film.

3. 18-8 regains passivity slowly in oxygen-free distilled water, rapidly in air-saturated water. The chromium-nickel steel containing molybdenum regains passivity rapidly in oxygen-free or air-saturated water. If a hydroxide film is hypothesized, its properties must be such that it forms slowly in absence of oxygen, but its formation must be speeded up by oxygen or by presence of molybdenum in the steel.

4. 18-8 treated with 6N HCl does not regain passivity in oxygen-free 4 per cent NaCl; the similar alloy containing molybdenum regains passivity slowly. If a hydroxide passive film be thought of as cause of passivity, the reason for lack of formation of the film on 18-8 in sodium chloride and its slow formation on 18-8 in water must be accounted for. Furthermore, the proposed cause must be compatible with the reason for the slow rate of formation of the supposed film on the alloy containing molybdenum in oxygen-free sodium chloride compared with its rapid formation in oxygen-free water. Any conceivable mechanism of hydroxide-film formation covering all these cases must necessarily be complex.

5. The ability of acids to destroy passivity depends not only on the pH but on the negative-ion constituent. Although this conclusion has been disclosed in the literature, it has not been previously pointed out that under some conditions acetic acid whose negative ion is much larger



than the chloride ion can at a specific equivalent pH produce greater activity of stainless steel than can hydrochloric acid. This result is not readily explained by an oxide or hydroxide film theory of passivity, which depends on the supposition that chloride ions being small can with greater ease than other ions penetrate the protective film. In this instance the larger ion is more effective. Other instances have been observed of the same kind; namely, the ability of larger bromide ions to react more readily with 18-8 containing molybdenum than the smaller chloride ions.<sup>14</sup>

### *Hydrogen Solution in the Lattice*

With an oxygen film ruled out by the experiments described above, the only film that can be hypothesized is the hydrated oxide or hydroxide film. But the hydroxide film is difficultly reconcilable with the facts; both with those described above and with those as a result of other type

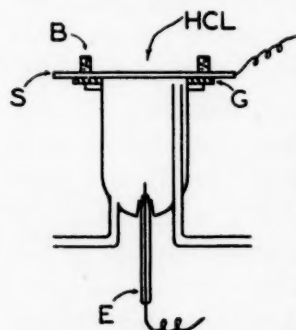


FIG. 6.—CELL FOR MEASURING POTENTIALS OF IRON CHARGED WITH HYDROGEN.

measurements, such as threshold potential and electron diffraction experiments.<sup>14</sup> Another explanation is possible, which has received experimental support in a study of passive iron, and has recently<sup>14</sup> been applied to the observations covering stainless steels and passive metals; that is, the hydrogen-solution theory first proposed by Grave and others<sup>15-18</sup> in observations on passive iron. It was proposed in their theory that a state of activity of iron existed when hydrogen was dissolved in the metal lattice, thereby "loosening" the metal atoms and causing chemical reactivity, whereas in the absence of hydrogen the metal was passive and less reactive. Several experiments were performed, which were consistent with this viewpoint but not with the oxide-film theory.

When hydrogen dissolves in iron there is no doubt that the chemical potential and reactivity of iron is affected. We proved this to our own satisfaction by setting up a cell similar to our previous cell (Fig. 6). The potential of iron specimen *S* (0.004 in. thick) was measured in oxygen-free 4 per cent NaCl contained in the closed cell, into which dipped an Ag-AgCl electrode *E*. A greased rubber gasket *G* made the entire cell airtight. Dilute hydrochloric acid could be poured on the iron specimen, as shown within a ring of molding clay *B*, and allowed to react with the upper side of the metal. The potential of the opposite side of the iron sheet was then followed with the potentiometer. When acid came in contact with the iron specimen, the potential of the opposite side became more active almost immediately. When the acid was washed out with



water, the potential fell to near its original value. During the acid treatment hydrogen bubbles came off the upper side freely, but it was observed that in addition hydrogen gas in small bubbles slowly appeared at the under side of the specimen within the cell. The hydrogen gas had diffused through the thickness of iron sheet. The potentials as affected by additions of acids or alkalis to the top surface of the iron specimen are plotted in Fig. 7. Similar results for cathodically polarized iron have been reported by Rathert.<sup>17</sup>

#### *Hydrogen Solution Applied to Stainless Steels*

The change of potential or activity of iron by solution of hydrogen in the lattice analogously can be the main cause of the destruction of passivity in stainless steels (chrome as well as chrome-nickel steels) by

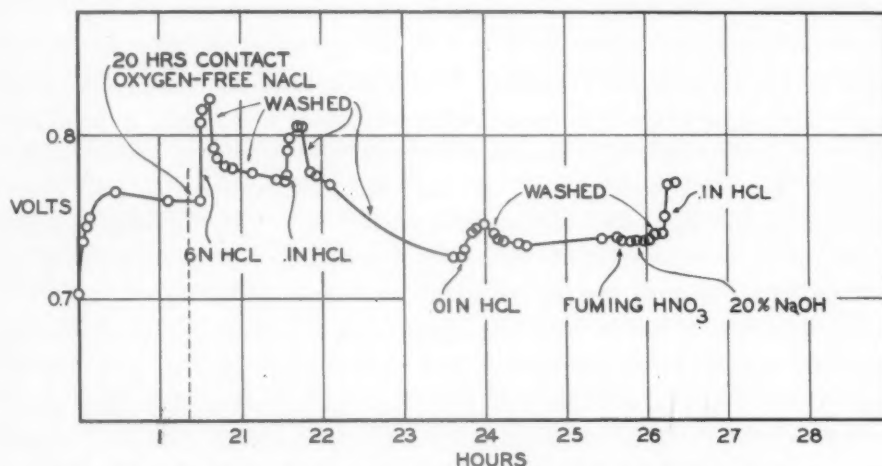


FIG. 7.—TIME-POTENTIAL DATA FOR IRON CHARGED WITH HYDROGEN.

acid treatment. The diffusion of hydrogen through a major thickness of chrome steel is too low for an experiment similar to the iron experiment of Fig. 6 to be performed easily, but there is no reason to believe that hydrogen cannot and does not dissolve at least in the surface layers of the alloy atoms when the alloy reacts with acids or is cathodically polarized. According to our picture, recently proposed<sup>14</sup> for passive alloys, hydrogen dissolves in the alloy as protons, the electrons being immediately available to displace electron bonds between chromium and iron and to fill unoccupied energy levels of both iron and chromium. The occupancy of these energy levels gives rise to active iron and chromium, which have electrochemical potentials near that of zinc and are readily reactive. When the hydrogen is removed by oxidation through contact of the alloy with air or nitric acid, the alloy again assumes the passive, nonreactive state with an electrochemical potential near that of silver.

Applying this picture to the results recorded in this paper, a consistent viewpoint is possible, somewhat more plausible than the viewpoint of the hydroxide film, and which can be correlated with passive phenomena in general. The reason that acid-activated 18-8 becomes passive in oxygen-free water, according to this viewpoint, is that hydrogen charged into the lattice by acid reaction diffuses out of the metal into the water, thereby allowing the alloy to revert to its passive state. This, in common with many diffusion processes, is naturally slow. In the presence of oxygen of the air, however, the hydrogen is catalytically and rapidly oxidized at the surface to water. This rapidly removes hydrogen and the steel quickly assumes its normal passive state. In the presence of oxygen-free sodium chloride an additional situation exists. The salt solution, unlike water, is a good conductor, so that electrolytic processes not possible in water can take place at the surface. Microscopic anodic and cathodic areas, which play a role in the acid pickling of stainless steels, can continue to function in sodium chloride with consequent evolution of hydrogen at the cathodic areas and continued activation of passive atoms. The rate of reaction may be slow, but the amount of hydrogen liberated exceeds the amount that diffuses away and is sufficient to keep the 18-8 steel in its active state. Even in the presence of air, the rate of liberation exceeds the rate of oxidation of hydrogen, so that the steel becomes only partly passive.

The reaction of acids with stainless steel exposes the anode-cathode areas that account for the continued activity of 18-8 in contact with oxygen-free sodium chloride. If the steel is, however, initially passive and then allowed contact with aerated sodium chloride, the steel becomes more passive with time, the potential reaching a final limiting value as shown in Fig. 3. This probably means that electrolytic action is not as readily induced in steels untreated with acid beforehand and that what little hydrogen is liberated by slow corrosion, slower than from acid-treated specimens, is readily oxidized. The lack of hydrogen preserves the passive state of the alloy surface, but slow corrosion constantly eliminates anodic areas responsible for the corrosion that takes place. With the disappearance of anodic areas, which are naturally more active, still less hydrogen is formed and the steel tends to become more noble in potential as observed.

If the steel is initially in contact with oxygen-free sodium chloride before acid treatment, the potential tends slowly toward an active value. This is probably again a question of electrolysis set up by galvanic currents at anode-cathode areas, which generate hydrogen and slowly destroy passivity. Unlike the case discussed in the preceding paragraph, no oxygen is present to assist in disposing the hydrogen, hence the metal gradually becomes more active. This fact must be coupled with the underlying reason for the marked tendency of stainless steels and

other passive alloys to corrode in stagnant salt waters or in protected areas of moving waters (contact corrosion). The corrosion is always more severe than in rapidly moving aerated solutions. Stagnant solutions can produce the active alloy observed in our potential measurements, which, markedly differing in potential from passive metal, gives rise to high-order corrosion currents at the expense of the active metal. In practice, pits or corroded areas are commonly found at places where the solution in contact has been stagnant. The lack of reproducibility of the initial potentials recorded in Fig. 2 can be attributed to variation in the galvanic currents accounting for activity and also to adsorbed oxygen films, which there is good reason to believe exist on the surfaces of all metals and which take time to dissipate either by diffusion or corrosion processes at the surface. This oxygen film is not in any way supposed to be a cause of passivity; in fact, the steel remains passive in its absence. Whatever role it plays in passivity, must, in connection with stainless steels, be minor or secondary, as the potential data given above point out.

Occasionally a specimen is chosen that becomes more active rather than more noble in aerated sodium chloride; i.e., specimens recently pickled or particularly inhomogeneous. The reason for the behavior of the pickled specimens follows from the discussion above. For the inhomogeneous specimens, the mechanism possibly lies in the accelerated electrolytic action caused by the inhomogeneities, which produces hydrogen and consequent activation. From a practical standpoint, these results indicate that pickled steel should first be passivated or exposed to air for some hours before immersion in a conducting solution or contact with corrosive environments, if corrosion is to be minimized. The pickling of steels charges hydrogen into the surface, which increases the reactivity of the steels, whereas exposure to air or treatment with nitric or chromic acids removes the hydrogen by oxidation.

The alloy containing 3 per cent Mo acts similarly to 18-8 but shows consistently a more stable passive state and a greater tendency to recover passivity. The anode and cathode areas for this alloy appear less active, as judged by our observations of the slow rate of pickling of the alloy containing molybdenum in hot hydrochloric acid as compared with 18-8 free of molybdenum. The relative lack of electrolytic surface action explains the ability of chromium-nickel-molybdenum steel to become slowly passive in oxygen-free 4 per cent NaCl and to rapidly regain complete passivity in air-saturated 4 per cent NaCl. Not enough hydrogen is generated by anode-cathode areas in the salt solution, nor hydrogen enough retained at the surface layers, to preserve the active state. The alloy therefore tends to become passive.

The same mechanism can account for the passivity destroying property of 20 per cent NaOH. By galvanic action hydrogen is liberated by

strong alkalies, producing active alloy at the metal surface, but hydrogen deposition is effectively prevented by the presence of an oxidizing material like  $\text{KMnO}_4$ , in the latter instance the metal remaining passive.

The effect of pH and negative-ion constituent is probably a question of rate of reaction. Unless the activity of the hydrogen ion is sufficient, no reaction with the stainless steel takes place, hence the steel is not activated by dilute solutions of hydrochloric acid. Ferrous chloride and other acid chlorides activate stainless steel, probably because of hydrolysis of the salts yielding appreciable concentrations of hydrochloric acid. The inactivity of potassium acid phthalate is probably explained by the mechanism of inhibitor action as contrasted with passivation, which terms the author prefers to define separately. Potassium acid phthalate presumably forms an iron compound or adsorbed layer of phthalate ions at the surface, which prevents further reaction. Such layers do not of themselves markedly affect the electrochemical potentials of the underlying metal,<sup>9</sup> whereas passivation processes always do. No reason is apparent at present for the differing degrees of activity in stainless steel produced by various concentrations of hydrochloric acid and acetic acids.

The data indicate that unexpected activation by certain media can occur, which, it is reasonable to assume, must be an integral part of the corrosion mechanism in such media. It should not be impossible, therefore, with the further development of the potential technique described above, to rapidly outline beforehand much desired information on the corrosion behavior of specific solutions in contact with passive alloys.

#### SUMMARY

The potential-time curves in 4 per cent NaCl free of oxygen were determined for 18-8 and the similar alloy containing 3 per cent Mo after activation of the alloy with 6N HCl for 10 min. Similar data were obtained for the two activated alloys in aerated sodium chloride and water, and in oxygen-free water. It was found that whereas activated 18-8 remained active, the alloy containing molybdenum slowly recovered passivity in 4 per cent NaCl *in the complete absence of oxygen*. Furthermore, the 18-8 alloy slowly recovered complete passivity in oxygen-free water. It was concluded, therefore, that any hypothesized film on stainless steels cannot be a molecular oxygen film.

In aerated sodium chloride, the alloy containing molybdenum recovered passivity rapidly whereas 18-8 recovered passivity only partially. In aerated water, 18-8 recovered passivity rapidly. The data point to the action of molybdenum in stabilizing passivity in chromium-nickel steels and to the action of sodium chloride in diminishing or inhibiting the transformation from the active to the passive state. It was observed that a steel not recently pickled or acid-treated, and for



the most part free of inhomogeneities, becomes more noble with time and reaches a final steady potential.

Potential-time curves in oxygen-free sodium chloride were obtained for chrome-nickel steel (19-9) containing varying percentages of molybdenum. These data show that for the alloy used, containing 0.05 per cent carbon, there is no appreciable effect in the stabilization of passivity below 2.00 per cent Mo; that is, the alloys did not recover passivity in 4 per cent NaCl in the absence of oxygen. From 2.00 to 3.50 per cent Mo, the data reveal stabilization of passivity with practically similar potential behavior for all the alloys.

It was found that treatment with nitric acid or with 20 per cent NaOH containing  $\text{KMnO}_4$  produces a more noble potential in stainless steels, whereas hydrochloric acid, acetic acid, saturated ferrous chloride and 20 per cent NaOH solutions produce an active potential. Active potentials were also measured for stainless steel treated with hydrochloric and acetic acids of various concentrations and pH. Hydrochloric acid, 0.001N, produced activity, but 0.0001N in concentration failed to destroy passivity. Acetic acid at a pH equivalent to 0.0001N HCl (4.09) is able, on the other hand, to produce activity.

Chromium, nickel and iron like 18-8 are activated by acid treatment and become passive by contact with oxidizing agents. Chromium, like the chromium-nickel steel containing 3 per cent Mo, rapidly loses activity even in the complete absence of oxygen. Platinum subjected to the same acid treatment shows only small changes in potential.

All these results are given reasonable interpretation on the basis of solution of hydrogen in the metal lattice. This theory assumes, based on definite experimental proof in regard to iron, that when hydrogen enters the lattice of the alloy the latter becomes electrochemically active. When the hydrogen is removed by diffusion, or oxidation by the air or oxidation by nitric acid, the alloy again becomes passive. This theory does not rule out the possible presence of films on the surfaces of stainless steels or chromium, but makes their presence either unessential or of secondary importance in accounting for passivity in these metals.

From a practical standpoint, the potential data indicate the advisability of air-exposing for some hours, or passivating stainless steels in an oxidizing solution after the pickling operation. The stainless steels in this manner are made passive (corrosion resistant) and tend to remain so in aerated salt solutions, whereas this may not be true if pickled steels are immediately immersed in a corroding solution.

#### ACKNOWLEDGMENTS

The author expresses his appreciation for the advice and support given this investigation by members of The Corrosion Committee at The Massachusetts Institute of Technology appointed to supervise the research



concerning the pitting of stainless steels for The Chemical Foundation. In addition, he expresses appreciation for the Committee's action in making available the able assistance of Dr. Arthur J. Miller in carrying out the experimental program.

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#### DISCUSSION

(Lewis E. Bergen presiding)

M. G. FONTANA,\* Buffalo, N. Y.—Are we to infer from the data shown that 18-8 equipment would deteriorate rapidly in 20 per cent NaOH? It is realized, of course, that actual service conditions would be different from those under which the data were obtained. The activity shown by the 18-8 in this caustic solution is quite surprising.

Would exposure to the air after immersion of the 18-8 specimens in hydrochloric acid or sulphuric acid result in passivation? In other words, if the 18-8 specimens were washed and dried after the time-potential data had been obtained, and then rerun without any further surface treatment, would the time-potential data obtained be the same?

Investigations like the one described in this paper are of great interest and value to us whose interest concerns the application of stainless steels in the chemical industry.

J. J. B. RUTHERFORD,† Beaver Falls, Pa.—The ingenious cell devised by Dr. Uhlig to determine the effect of the diffusion of hydrogen through iron on the potential as measured in oxygen-free sodium chloride solution, from which an analogy has been derived and applied to stainless steels, would not necessarily function in the same manner if a stainless-steel sheet were substituted for the iron sheet, even on making

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allowance for differences in rate of hydrogen diffusion. It is highly undesirable to argue from analogy where direct experimental proof can be readily obtained. Similarly, the author's experiments with acetic acid are difficult to reconcile with the fact that quantities of 18-8 (the molybdenum-containing alloy is preferred) are used in the manufacture of acetic acid, representing wide variations in temperatures, acid concentration and oxygen concentration, with eminent success.

On acid-pickling carbon steels, it is necessary to bake for a few hours at about 100°C., otherwise the condition of "hydrogen-embrittlement" might exist for days at room temperatures. It is difficult, therefore, to reconcile this evidence with the theory that hydrogen dissolved in stainless steel, notoriously more sluggish, is "neutralized" almost instantaneously on exposure to air or oxygen-bearing salt solution.

Many other data than potential measurements from one basic experiment should be required to nullify a hypothesis of such wide scope as the oxygen-passivation theory. From a single experimental technique, it is necessary to guard against manipulative phenomena that are readily subject to misinterpretation. For example, in the experiments described, the specimen under study is an integral part of the container system; our experience would suggest the initiation of contact corrosion between the gasket and the specimen, particularly in the presence of activating solutions, which could not readily be remedied by merely substituting a passivating reagent but would continue to affect the potential measurements. We suggest that the author examine closely his specimens and determine the relative ratio of dissolution at the freely exposed area and the area approaching contact with the gasket. A combination of the effect just described and the nature of the equipment in retarding replacement of the various media may account for the apparent discrepancy in the time interval required for passivation as recorded here in hours and elsewhere in seconds.

U. R. EVANS, \* Cambridge, England.—Dr. Uhlig's experiments and conclusions will be read with interest, even by those who do not accept all his arguments against the importance of films in passivity. But probably most will agree that both the internal state of the alloy and the specific nature of the anions are extremely important factors in deciding the chemical resistance; indeed, this is true whether a film imposes a perceptible restraint or not, since, in the modern views of protective films,<sup>19</sup> the affinity between the metal and nonmetal (or anion) enters into the mathematical expression for the rate of passage through the film.

Probably few people still believe that the difference between activity and passivity consists in the absence of oxide on the active metal and its presence on passive metal. It has been shown by several different methods that practically all metals exposed to air soon become oxidized superficially. The time-thickness curves published recently by Dr. Miley and myself<sup>20</sup> show that even at ordinary temperatures the initial rate of oxidation of iron or copper is very rapid, but it soon falls off as the oxide begins to isolate copper and oxygen from one another; at higher temperatures, where diffusion through the film is possible, thickening continues, and interference colors are produced. If, then, films are always present, the existence of a film cannot be the sole criterion of passivity. It is rather the state of the film that is an important factor, deciding whether attack will continue or smother itself. This is well brought out in W. J.

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\* Cambridge University.

<sup>19</sup> See, for instance, T. P. Hoar and L. E. Price: *Trans. Faraday Soc.* (1938) **34**, 867.

<sup>20</sup> U. R. Evans and H. A. Miley: *Nature* (1937) **139**, 283.

H. A. Miley and U. R. Evans: *Jnl. Chem. Soc.* (1937) 1295.

The rapid initial oxidation, soon slowing down, is also shown optically by A. B. Winterbottom: *Nature* (1937) **140**, 364.

Müller's work. (Like many of the other European authors quoted by Dr. Uhlig, Müller has published many papers more recent than the one cited in the list of references.) Müller<sup>21</sup> lays great stress on the pore size, but obviously the environment is also important; pores large enough to permit attack in some solutions will become blocked up in other solutions.

The idea that there is more film material on passive metal than on active metal is often the reverse of the truth. If the conditions are such as to produce the film material in a compact form, it will stifle its own growth when very small amounts are present; thus the films present on austenitic stainless steel appear to be thinner, not thicker, than those on ordinary steel. Fourteen years ago,<sup>22</sup> I found that copper that had been charged with hydrogen by cathodic treatment in sodium hydroxide was oxidized rapidly by dissolved oxygen, so that interference tints appeared at ordinary temperatures in the same sequence as would otherwise be obtained on exposure to air at high temperatures. The probable explanation is that the hydrogen keeps the film porous and permits continued growth; the porosity may be due either to alternate oxidation and reduction (as in the formation of a lead accumulator plate), or to the swelling up of the metallic lattice, owing to the hydrogen, which will lead to an oxide film more distended than that formed on hydrogen-free copper. Perhaps the effect of hydrogen on iron, observed in Dr. Uhlig's experiments, may be somewhat similar. But the possibility that the hydrogen, by swelling the metal, will directly loosen the metallic atoms need not be excluded in either case.

Dr. Uhlig urges that neither iron hydroxide, nickel hydroxide, nor chromium hydroxide possesses the chemical properties needed to explain the passivity of austenitic stainless steel. But it is necessary to consider the possibilities of mixed oxides or hydroxides, and also solid solutions of oxides or hydroxides. The equilibrium diagram of oxide systems is not always well known, but it may sometimes prove to be as complicated as the equilibrium diagram of metallic alloys. In any case, this sort of argument is open to objection, since the properties of a substance in the film condition are sometimes different from those in the state in which it is commonly met with.

It used to be argued that passivity of ordinary iron could not be connected with the formation of an oxide film, since passivity could be produced by anodic treatment in sulphuric acid, which—it was alleged—would dissolve all known oxides of iron. Actually I found<sup>23</sup> that ferric oxide films isolated by undermining, either from passive iron or from heat-tinted iron, were *not* destroyed on standing in dilute sulphuric acid, provided that they were out of contact with the metal. The rapid destruction of these oxide films when they were in electrical contact with the metal was due to the formation of short-circuited cells, which caused reduction from the insoluble (ferric) to the freely soluble (ferrous) state.

Nevertheless, it is extremely likely that the affinity between the various constituents of an alloy may be an important factor in deciding its chemical stability. If the attraction between unlike atoms exceeds that between like atoms, the mean work of mutual separation of atoms in the alloy may exceed that in either pure metal, so that the alloy may be both mechanically stronger and chemically more resistant than its constituents. (This may operate either in the absence of a film, or as a factor determining the probability of penetration through the weak points of a film—if one is present.) I have suggested<sup>24</sup> on such lines an explanation for the high chemical

<sup>21</sup> W. J. Müller: *Ztsch. Elektrochem.* (1934) **40**, 119; *Korr. Met.* (1932) **8**, 258; (1935) **11**, 31.

<sup>22</sup> U. R. Evans: *Jnl. Chem. Soc.* (1925) 2484.

<sup>23</sup> U. R. Evans: *Jnl. Chem. Soc.* (1930) 478.

<sup>24</sup> U. R. Evans: *Corrosion, Passivity and Protection*, 419. New York, 1937. Longmans Greene and Co.

stability of iron-nickel alloys to acids. It might at first sight appear that that type of explanation could not be applied to cases where one of the alloying constituents is present in only small amounts, but the work of Dobinski<sup>25</sup> suggests that the proportion of the two constituents in the external layer may be very different from that in the bulk of the metal.

Most of the recent work carried out at Cambridge (England) whether based on the statistical study of large numbers of drops<sup>26,27</sup> or on the velocity of film growth,<sup>28</sup> or on the movement of potential with time,<sup>29</sup> indicate that, in the particular cases studied, the chief factor is the resistance of the skin (not necessarily an oxide film) toward passage through it. But this is itself dependent on the nature both of the metallic phase and of the solution, and we can confirm Dr. Uhlig's statement that it is not always the smallest ions that are most effective in breaking down passivity; sulphates added to an inhibitive solution may cause a higher probability of corrosion than similar additions of chloride, although the attack remains more localized (p. 534 of ref. 26). One must not neglect the possibility of the existence of cases where the film-factor may be less important than the external or internal factors, or even absent altogether; doubtless in due course an equation will be produced expressing the effect of all three sets of factors on the probability of attack.

T. P. HOAR,\* Cambridge, England.—In this and previous papers, Dr. Uhlig has adumbrated a novel theory of passivity, which he considers better able to explain the facts than the usually accepted "oxide-film" theory. The new theory states that iron and chromium are made "active" by the presence of atomic hydrogen, and that when this is removed by oxidation the pure metal is in the "passive, non-reactive state with an electrochemical potential near that of silver" (p. 399). Herein lies the weakness of Dr. Uhlig's theory: its fundamental postulate is that *iron and chromium are metals as noble as silver*—although their oxides and compounds generally are comparatively difficult to reduce to metal (cf. silver oxide, decomposed on gentle heating, etc.). Indeed the whole thermochemistry and thermodynamics of the metals show that the idea of "noble" iron and chromium cannot be sustained.

Though this point alone is, in my view, sufficient to invalidate Dr. Uhlig's theory of passivity, it may be well to show that his five points on p. 397 can be readily explained on the oxide-film theory, thus:

1. The regaining of passivity in aqueous solution in the absence of oxygen is due to the formation at the anodic points of an oxide or hydroxide film by an anodic reaction of the type  $\text{Me} + 2\text{OH}^- \rightarrow \text{MeO} + \text{H}_2\text{O} + 2\epsilon$ , the cathodic reaction being  $2\text{H}^+ + 2\epsilon \rightarrow \text{H}_2$ . Such reactions are possible for both iron and chromium in solutions of pH 7.

2. If the film on stainless steel consists of or contains  $\text{Cr}_2\text{O}_3$  or  $\text{Cr}(\text{OH})_3$ , 20 per cent NaOH will destroy passivity by dissolving or peptizing this; presence of potassium permanganate, however, will produce a protective film of  $\text{MnO}_2$ . Subsequent treatment in nitric acid, though it may well remove the  $\text{MnO}_2$ , will not prevent the re-formation of a  $\text{Cr}_2\text{O}_3$  film, and the metal remains passive.

3. The formation of oxide or hydroxide films at anodic points is hastened by the presence of oxygen, because the oxygen acts as a cathodic reactant; e.g.,  $\text{O}_2 + 2\text{H}_2\text{O} + 4\epsilon \rightarrow 4\text{OH}^-$ , or  $\text{O}_2 + 4\text{H}^+ + 4\epsilon \rightarrow 2\text{H}_2\text{O}$ . Thus the anodic change given above under 1 is speeded up. The action of molybdenum is discussed in the next paragraph.

<sup>25</sup> J. Dobinski: *Nature* (1938) **141**, 81.

<sup>26</sup> R. B. Mears and U. R. Evans: *Trans. Faraday Soc.* (1935) **31**, 527.

<sup>27</sup> R. B. Mears: *Iron and Steel Inst. Carnegie Schol. Mem.* (1935) **24**, 69.

<sup>28</sup> L. E. Price and G. J. Thomas: *Jnl. Inst. Metals* (1938) **63**, 21, 29.

<sup>29</sup> T. P. Hoar and U. R. Evans: *Jnl. Iron and Steel Inst.* (1932) **126**, 379.

\* Metallurgical Laboratories.



4. The presence of chloride ion in the electrolyte always militates against passivity, because it allows the electrolyte at the bottom of a pore in the film to become acid; owing to the "transport number" effect of the excess  $\text{Cl}^-$ , the cathodically produced  $\text{OH}^-$ , outside the pore, does not migrate inward quickly enough to replenish the  $\text{OH}^-$  discharged at the pore base, and acidity results. Now "active" 18-8 (at the bottom of the pore) will go into solution easily in acid; and according to the reaction  $\text{Me} \rightarrow \text{Me}_{\text{aq}}^{++} + 2e$ ; and the rate of this reaction relative to that of  $\text{Me} + 2\text{OH}^- \rightarrow \text{MeO} + \text{H}_2\text{O} + 2e$  will determine whether film breakdown or repair takes place—the former reaction producing "undermining" and the latter "plugging" of the film. Now steels containing molybdenum are well known for the slowness of their attack by acids even when they are in the "active" state—ordinary mild steels containing small amounts of molybdenum, though by no means "stainless," are much more resistant to acid attack than molybdenum-free steels. Thus we may expect the reactance  $\text{Me} \rightarrow \text{Me}_{\text{aq}}^{++} + 2e$ , at the bottom of a pore, to be reduced in rate by the presence of molybdenum; undermining is therefore not favored, and film formation is easier.

5. The acid anion is always important in destroying passivity, not only because of film penetration, but also because of direct film dissolution. Any anion that forms a soluble and stable complex anion with the metal tends to dissolve the oxide or hydroxide according to ordinary solubility-product principles. Thus acetates, and especially citrates, tartrates, etc., are often very effective in destroying passivity, owing to the very stable complex metallic anions that they form. The effect of the bromide likewise may be due to complex anion formation.

The hydrogen-diffusion experiments are easily explained if we suppose the oxide film on the far side to be reduced by the diffusing atomic hydrogen: Morris<sup>30</sup> showed that when hydrogen diffuses through iron, of which the far side is in contact with moist air, comparatively thick oxide films showing interference tints are formed, doubtless because the continual reduction and reoxidation produces a porous film that can grow readily.

R. B. MEARS, \* New Kensington, Pa.—It is fortunate that Dr. Uhlig has been able to continue his interesting and valuable studies on the mechanism of corrosion of stainless steel. Accurate data of the type presented in his paper are all too uncommon in this field of research.

The theory of passivity presented by Uhlig and Wulff in an earlier paper (ref. 14) and enlarged upon in the present paper has some points that commend it. Nevertheless many of the data cited by the author as evidence against the older oxide coating theory can be interpreted as supporting the oxide theory. The fact that 18-8 stainless steel containing molybdenum regains passivity in 4 per cent NaCl solution in the absence of dissolved oxygen is easily explained by the oxide theory. A considerable amount of work has established that ordinary iron can react with oxygen-free water to oxidize itself and free gaseous hydrogen. Thermodynamic calculations indicate that the reaction of iron with air-free water to form magnetite results in a decrease in free energy of 4430 cal. per gram atom of iron. The decrease in the free energy for the formation of  $\text{Cr}_2\text{O}_3$  from chromium in air-free water is even greater. Thus it appears entirely reasonable to suppose that the reason the 18-8 steel containing molybdenum regains passivity in oxygen-free sodium chloride solution is simply that it decomposes sufficient water to oxidize its surface. (It is immaterial from the standpoint of the oxide film theory whether the film formed is an oxide, a hydrated oxide or a hydroxide.)

The authors have used time-potential curves to indicate whether or not the stainless steel was in the active or passive conditions. Such curves are useful provided the

<sup>30</sup> T. N. Morris: *Jnl. Soc. Chem. Ind.* (1935) **54**, 7T.

\* Metallurgical Division, Aluminum Research Laboratories.



mechanism of the corrosion reaction is known. However, if there is considerable anodic polarization of the local cell anodes, measurement of time-potential curves does not necessarily give an indication of change from passivity to activity or the reverse. This point is discussed in greater detail in a recent paper by Mr. Brown and myself.<sup>31</sup>

H. H. UHLIG (author's reply).—In answer to Dr. Fontana, there is not necessarily an indication that 18-8 would deteriorate rapidly in 20 per cent NaOH. On the other hand, there is indication that the alloy having lost passivity would corrode at a rate not far removed from the corrosion rate of iron in the same medium.

Exposure of 18-8 specimens, initially pickled in acid, to oxygen of the air results in complete passivation. Specimens so passivated we found to behave in our potential measurements comparable with abraded surfaces. Only in contact with 4 per cent NaCl did 18-8 remain partially active after pickling.

Mr. Rutherford's remarks concerning the question of presenting an analogy in the diffusion of hydrogen through mild steel with the behavior of stainless steels toward hydrogen can happily be answered with experiment. We have recently succeeded in detecting the diffusion of hydrogen through sheets of chromium-iron alloys 0.045 in. thick, with chromium content varying from 5.4 to 20.3 per cent. At chromium contents above approximately 11 per cent, hydrogen diffusion is slower than for mild steel, but there is no doubt that in a matter of hours the hydrogen diffuses through these steels in a manner similar to its diffusion through iron. The same cell was used as described above, using as source of hydrogen cathodic discharge in a 0.1N H<sub>2</sub>SO<sub>4</sub> solution. Evidence from potential measurements shows that the surface hydrogen of stainless steels is oxidized rapidly on exposure to air.

Research workers in the field of corrosion have used the electromotive series to indicate which metal in a galvanic couple corrodes preferentially in some specified corroding agent. A metal like iron is considered cathodic to or more noble than zinc, whereas iron is anodic to or less noble than copper. This concept is useful in explaining the protective action of galvanized coatings and accelerated corrosion of porous copper plates on iron. A solid solution alloy, likewise, can be cathodic to or more noble than a pure metal that finds a position in the electromotive series. Some metal in the series will be found by potential and corrosion experiments neither anodic nor cathodic to the alloy, so that one can say that the alloy is "as noble" as the metal with which it compares. If the alloy is coupled to this metal in an electrolyte like sea water, no electric current will flow and there will be no preferential corrosion of one component of the couple. It is in this sense that 18-8 is said to be "as noble" as silver. There is no implication, as Dr. Hoar intimates, that all the chemical properties of 18-8 and silver are identical; only the practical indication is pointed out that their respective tendencies to dissolve in certain solutions are nearly identical.

There is no reason to believe that a hydroxide film is impossible on stainless steels. The mechanism for formation of such a film is straightforward and it is plausible that such a film might be detected using a sufficiently refined technique similar to that of Dr. U. R. Evans (p. 53 of ref. 24) and his students. Attributing to this film, however, properties that account for passivity and activity of 18-8 is one magnitude removed as a plausible concept and falls short of being the simplest explanation for the facts of passivity.

If one takes stainless-steel corrosion products and produces corresponding oxides or hydroxides by adding sodium hydroxide solution, addition of nitric acid again dissolves the hydrated chromium oxide as well as the iron and nickel oxides. No precipitate of Cr<sub>2</sub>O<sub>3</sub> remains. Furthermore, experiment indicates that nitric acid also dissolves precipitated manganese oxides, so that MnO<sub>2</sub> cannot reasonably be a protective film on a metal resistant to nitric acid. The contention that fused or

<sup>31</sup> *Trans. Faraday Soc.* (1939) **35**, 467.

dehydrated oxides of chromium or manganese are known to be relatively insoluble in nitric acid cannot apply here, because surface hydroxides, if present, must have formed at room temperature in the absence of dissolved oxygen and in the presence of excess water favoring hydration. The hydrated oxides on the surface therefore should be soluble in nitric acid unless properties of these surface oxides are inconsistent with properties of oxides precipitated in the body of a solution.

On the basis that hydrogen solution in the surface lattice accounts for loss of passivity, inconsistencies with our knowledge of conventional chemical facts do not appear. Sodium hydroxide reacting with a metal forms hydrogen which is considered to activate the metal, but in the presence of permanganate is prevented from doing so by oxidation of the hydrogen or depolarization of the metal surface.

We have had no indication that bromides form complexes with constituents of stainless steels. Threshold potential data show that 18-8 in bromide and chloride solutions, and Mo 18-8 in bromide solutions behave similarly, but that Mo 18-8 in chloride solutions shows abnormally high breakdown. 18-8 correspondingly pits in ferric bromide and chloride, but Mo 18-8 pits in ferric bromide, not in ferric chloride (4-hr. test, 10 per cent solution). The behavior of Mo 18-8 is outstanding, therefore, in chloride solution rather than in bromide solution. Molybdenum itself does not appear responsible for an unusual film formation because the pure metal in either chloride or bromide solution corrodes anodically as molybdenum oxide.

Concerning Dr. Hoar's explanation of the effect of diffused hydrogen in reducing a supposed passive film, the explanation is weakened as in the case of the lack of solubility of oxide films in acid, by our knowledge that oxides like  $\text{Cr}_2\text{O}_3$  are difficultly reducible by hydrogen under any condition. But were this reduction possible, it must be borne in mind that hydrogen available through the reaction



and formed in the very process that produces the metal oxide would also be then available to reduce the same oxide film on the surface.

The real value in any discussion of mechanism of this kind is the amount of experimental work it eventually inspires, since difference of viewpoint is more decisively settled in the laboratory than elsewhere. We have good reason to believe that an electron-sharing concept of passivity in alloys accounts for and will account for experimental facts not explained by any of the viewpoints of passivity so far proposed. It was never our intention, however, that the role which oxide films play in general corrosion phenomena should be ignored.<sup>32</sup> It is gratifying, therefore, to have Dr. Evans' comments, in which he emphasizes that a combination of factors within the metal as well as environmental factors seem best adapted to explain the phenomena before us. With this viewpoint we are in hearty accord.

For some metal systems it appears that the film serves a function more important than any other factor in corrosion protection. It is our belief, however, that in alloys like stainless steels, the protection afforded by an oxide film, if such is present, is secondary and that the reasons for the passive nature of such steels reside in a change in reactivity of the metal itself brought about by electronic changes in alloying. Hydrogen entering the metal lattice, we believe, can alter the reactivity. Dr. Evans and his students in investigations admired by every one who is familiar with their many publications have shown the role which films play in corrosion phenomena. In any equation, however, which Dr. Evans awaits to take care of the various factors influencing corrosion of metals we still expect oxide films to play an unimportant role for solid solution alloys of the transition group elements herein described.

<sup>32</sup> See discussion, *Trans. A.I.M.E.* (1939) **135**, 530.

## Pitting of Stainless Steels

By H. H. UHLIG\*

(Chicago Meeting, October, 1939)

SOON after general use of stainless steels began, it was observed in practice that certain combinations of factors tended to induce corrosion by pitting. For most applications this was a serious drawback, not so much because the structural properties of the metal were impaired but because of the rapidity with which heavy sections of the alloys were penetrated by small elongated pits. These pits seemed to initiate readily in oxidizing metal salt solutions like ferric chloride and in chloride solutions like sea water. It was observed that in sea water pitting was more frequent in stagnant or polluted waters than in highly aerated, moving waters. The steels in these chloride solutions were observed to be sensitive to long contact with material such as sand grains or attached barnacles. At points of attachment or contact it was not uncommon to discover initiation of corrosion. Pits once begun at contact faces were observed to grow rapidly, usually elongating phenomenally in the direction of gravity until the metal was perforated. Hydrochloric acid and other nonoxidizing acids, on the other hand, were observed to corrode stainless steels generally; the weight losses often were higher, but the penetration less than for the pitting type of corrosion.

The causes of pitting, a type of corrosion recognized as characteristic not only of stainless steels but of many additional metals and alloys, are important in corrosion studies. A possible explanation bears practical significance, for once it is known why pits begin where they do and continue to grow after initiation, intelligent direction can be given to diminishing corrosion. This can be done either by some alteration in the composition and treatment of the alloy or by some alteration in the environment.

It appears foremost in importance to discover the nature of pit foci, for if initiation of pits can be discouraged their growth will be no longer a factor to be considered. In a multi-component alloy containing many impurities normal to production of such an alloy, each of which may play a part in pitting, and whose corrosion resistance is sensitive to heat-

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Manuscript received at the office of the Institute June 27, 1939; revised Sept. 26, 1939. Issued as T.P. 1150 in METALS TECHNOLOGY, April 1940.

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treatment, the problem from this standpoint is complex. Some initial research in this direction has been reported.<sup>1</sup> But were very pure alloys free of pit foci, which probably is not true, the difficulties of commercial production would eliminate this resort as a practical suggestion. From practical considerations, it would be important, in addition to diminishing pit foci, to diminish growth of pits initiating at these foci.

The approach to the problem of pitting by an attempt to inhibit growth of pits is one possibility, therefore. This approach would be facilitated by a knowledge of the underlying mechanism of pit growth. It is primarily with this aspect of the subject that this paper deals. In addition, a discussion is included of a possible mechanism of contact corrosion observed in passive alloys regardless of the presence or absence of pit foci.

Wesley and Lindsley<sup>2</sup> published a paper on pitting of stainless steels in which they showed that ferric salts could not be considered responsible for initiation of pits in sea water. The solubility of ferric hydroxide, they reported, was too small in a solution such as sea water with pH of approximately 8. The authors assigned more possible weight to the action of ferrous salts but offered no evidence that these enter into the mechanism of corrosion.

Evans<sup>3</sup> early published an account of the pitting of zinc immersed in chloride solutions, in which he showed that the metal of the pit was anodic and that a corrosion cell was established by differences in oxygen concentration outside and inside the pit. For stainless steels the situation appears analogous, although, as shown later, factors enter in addition to oxygen which make the pitting of passive alloys more probable and when occurring more severe.

#### CHEMISTRY OF THE PIT

The elongated pit or groove that was commonly found in sea-water service tests suggested the importance of the corrosion products as active agents in furthering corrosion. The elongated pit, we observed, always lengthened in the direction of gravity, and once begun did not, for example, show marked tendency to grow upward or sideward. If the specific gravity of the corrosion products were considerably higher than the corrodent, it would be expected that as they diffused out of a pit flow would be downward; new metal surface would then be contacted and other pits started, which eventually would become an elongation of the first. This process could conceivably continue until the corrosion products reached the bottom edge or surface of the metal. One possible explanation for the specific action of the corrosion products on the metal was an electrolysis set up by a cell formed from the materials inside and outside the pit.

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<sup>1</sup> References are at the end of the paper.



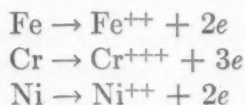
It is reasonable to suppose that the interior of stainless-steel pits are anodic, because metal dissolves to its ions in this region. The cathodic reaction products would form in the region outside and largely adjacent to the pit. The presence of oxygen or an oxidizing agent outside the pit, and a conducting solution comparatively free of oxygen or oxidant inside the pit, in itself would generate an appreciable electromotive force, although, as later described, the actual electromotive force is affected in addition by passivity and activity of the metal.

The action we have assumed to take place is illustrated in Fig. 1. Ferric chloride, used as corrodent, is outside the pit in contact with the metal surface acting as the cathode of the cell; ferrous, chromic, and nickel chlorides formed by solution of the metal are retained in the pit in contact with the metal surface acting as the anode. As the cell operates, electrons move through the metal from anode to cathode; chloride ions tend to move into the pit through the orifice. Ferrous ions ( $\text{Fe}^{++}$ ), chromic ions ( $\text{Cr}^{+++}$ ) and nickel ions ( $\text{Ni}^{++}$ ) are formed by solution of metal at the anode and  $\text{Fe}^{+++}$  ions are formed by reduction of  $\text{Fe}^{+++}$  at the cathode.

Although ferrous salts are produced at both anode and cathode, the distinguishing difference is that ferrous ions formed in the pit are largely retained, whereas ferrous ions produced at the large cathode areas readily diffuse away from the surface. The cathode reaction representing chemical reduction is



The metal in contact with the corrosion products, or metal chlorides in this case, tends to dissolve (corresponding to oxidation) to its ions in amounts proportionate to the original alloy composition:



The valences of the corrosion products given in these equations are known from analyses of anodic corrosion products of 18-8 stainless-steel electrodes electrolyzed in sodium chloride at current densities (0.01 amp. per sq. cm.) corresponding to rate of pit growth in accelerated tests using 10 per cent  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ .<sup>4</sup>

The presence of  $\text{Fe}^{+++}$  ions outside the pit and  $\text{Fe}^{++}$  ions inside is capable of generating sufficient electromotive force to account for corrosion at the pit, as we know from the high molal oxidation-reduction

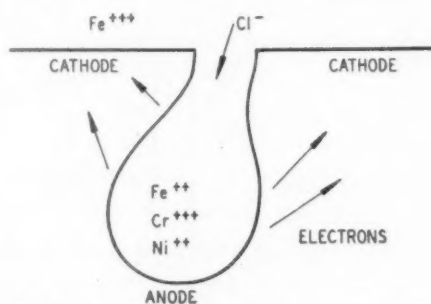


FIG. 1.—18-8 IMMERSED IN FERRIC CHLORIDE. DIAGRAM OF PIT.



potential of the  $\text{Fe}^{+++}$ ,  $\text{Fe}^{++}$  system ( $-0.77$  volt). This, however, as a motivating source of corrosion current is coupled with changes in the chemical reactivity or passivity of metal within the pit. We found that corrosion products enter the corrosion mechanism by making active any of the passive alloy with which it comes in contact, the activated metal remaining so for some time even after the corrosion products have been replaced by other solutions. This is the property not alone of ferrous chloride but of hydrochloric acid and all chlorides, particularly those free of oxygen, that are acidic by hydrolysis. Experimental indication of

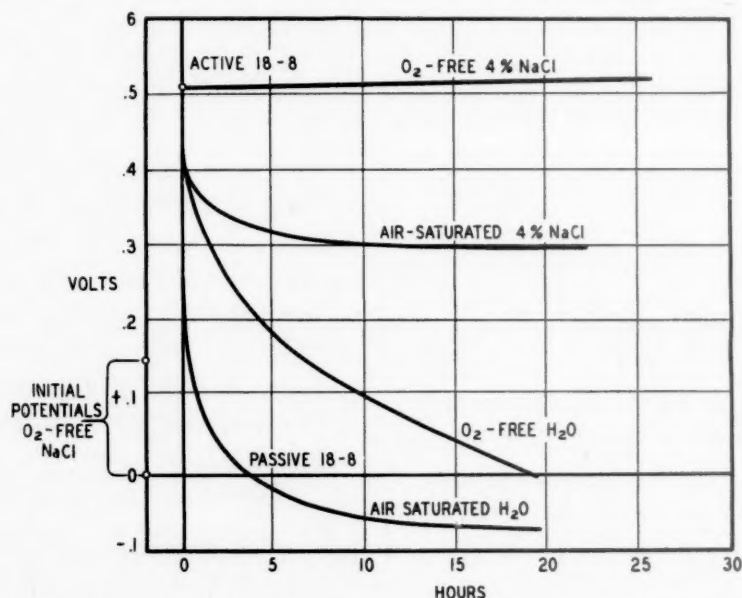


FIG. 2.—TIME-POTENTIAL MEASUREMENTS FOR 18-8 VS. SILVER-SILVER CHLORIDE.

this passivity-destroying property was obtained in potential measurements of stainless-steel surfaces. It was found that if ferrous chloride solutions or hydrochloric acid were allowed to remain in contact with the passive surface of 18-8 for a few minutes, the alloy lost passivity and became more active in the electromotive scale by 0.4 or 0.5 volt.<sup>5</sup> It was found that the alloy once activated retained activity in oxygen-free 4 per cent NaCl solution, and regained only partial passivity in air-saturated sodium chloride.\* Passivity is completely regained, however, when electrolytes are absent, as was shown for the steel immersed in aerated and oxygen-free water. Typical time-potential data for 18-8 measured against an Ag-AgCl reference electrode are reproduced in Fig. 2. The procedure in obtaining these data was to treat the 18-8 elec-

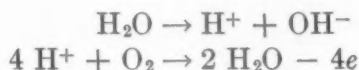
\* This was not true, however, of the similar alloy containing 3 per cent Mo. For this alloy passivity was entirely recovered, slowly in the absence of oxygen, rapidly in the presence of oxygen. This fact appears to be related to improved corrosion resistance of the molybdenum alloy to chlorides.

trode with 6N HCl for 10 min. to destroy passivity, wash the cell with oxygen-free 4 per cent NaCl, or aerated 4 per cent NaCl, or oxygen-free or aerated water for the time indicated, but always to measure the potential with the cell filled with oxygen-free 4 per cent NaCl. The initial potentials of the steel, as shown, varied between the passive potentials 0 to 0.15 volt. These were not as reproducible as the active potential, but the differences in potential between active and passive alloy were always considerable. This information is particularly useful applied to the mechanism of contact corrosion, discussed later.

The large potential difference between active metal of the pit in contact with the corrosion products and noble or passive metal outside the pit accounts for the large corrosion currents that cause rapid growth of the pit. The potential differences and resultant currents are larger than those observed in nonpassive metals like zinc, where differences in oxygen concentration alone account in the main for the corrosion observed. The potential difference of the active metal-passive metal cell is comparable to the iron-silver couple, hence it is not surprising that corrosion once initiated can be rapid, as is often observed in the pitting of these alloys.

The rate of corrosion is dependent on the efficiency of depolarization at the cathode areas. If ferric chloride is the corroding solution, all products at anode and cathode are largely soluble and readily diffuse. Electrons can be rapidly absorbed at the cathode area by  $\text{Fe}^{+++}$  ions making possible high corrosion currents.

If aerated sodium chloride is used instead of ferric chloride, the mechanism is similar although the corrosion is less rapid. The anode reaction involving solution of the metal is the same. The cathode reaction is:



or summing:



When oxygen is available this reaction proceeds as rapidly as oxygen can diffuse to the surface. The amount of oxygen dissolved in water is slight, however, so that depolarization takes place at a limited rate, and corrosion currents are likewise limited. In no instance is corrosion as rapid as with ferric chloride, which is a more efficient depolarizer.

If oxygen is not available, corrosion decreases almost to nothing. This low rate of corrosion is accompanied by slow evolution of hydrogen. Evolution of hydrogen in corrosion processes of ferrous metals in salt solutions is slow, owing, as has been pointed out in the literature, first to the extra potential or overvoltage necessary to liberate the gas, which diminishes the driving force or voltage available for the reaction, and, second, to the insulating effect of a layer of hydrogen bubbles over the

metal surface. In addition, whenever hydrogen is liberated on the surface of passive metals and alloys, the metal loses passivity and becomes active. (This effect is included in the so-called overvoltage effect.) This hydrogen can be supplied by acid reaction or by electrolysis in salt solutions in which the alloy is the cathode. In corrosion processes, hydrogen liberated at the cathode areas of passive alloys, if not oxidized, similarly activates the alloy. It would be expected, therefore, that passive alloys in salt solutions would no longer pit in the complete absence of oxygen, but would corrode slowly in general fashion. This, in fact, was indicated in an accelerated test in which stainless-steel 18-8 specimens, 5 by 1 by  $\frac{1}{8}$  in., immersed in 4 per cent NaCl at 90° to 100°C. into which nitrogen

was bubbled, lost an average of 0.15 mg. in 24 hr. and did not show any signs of pitting. Similar specimens in aerated 4 per cent NaCl lost 40 to 60 times as much weight and corroded by pitting.

With corrosion in alkali salt solutions there is accumulation of hydroxyl ions at the cathode areas. Metal chlorides diffusing out of the pit react with these alkaline corrosion products to form a ring of rust, mainly hydrated metal oxides, at the pit orifice. This is commonly observed in specimens corroded in aerated salt solutions.

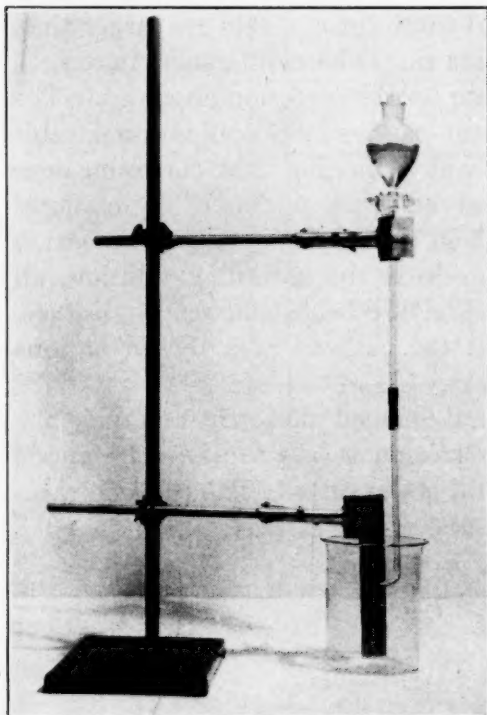


FIG. 3.—THE "STREAM-BEAKER" EXPERIMENT.

#### THE "STREAM-BEAKER" EXPERIMENT

From what has preceded, it appears plausible that reaction products maintain a difference in potential between the pit surface

and metal in contact with the corrodent outside the pit and that rate of pit growth depends on the efficiency of depolarization at the cathode areas. It was fairly easy to procure experimental evidence that this is so. In a first experiment, ferrous chloride and ferric chloride solutions were permitted to flow over a surface of stainless steel (18-8) in streams adjacent to each other and in contact but not mixing. Corrosion took place under the ferrous chloride stream as predicted.

A second experiment avoided some extraneous corrosion, which was always prevalent at the air-liquid interface, by flowing a fine stream of ferrous chloride onto stainless steel below the surface of ferric chloride

solution (Fig. 3). A 10 per cent ferric chloride solution, corresponding to the corrodent, is poured into the beaker until it covers 8 or 9 cm. of the steel specimen. Ferrous chloride corresponding to corrosion products inside the pit is contained in the dropping funnel. To produce downward flow of the ferrous chloride, its concentration is sufficient to give it a weight density appreciably greater than the ferric chloride solution in the beaker. The tip of the dropping funnel placed about 1 cm. below the surface of the ferric chloride is drawn to a small diameter and ground flat so that the ferrous chloride flowing very slowly from the funnel forms a stream about 1 mm. wide. This flows over the surface of the

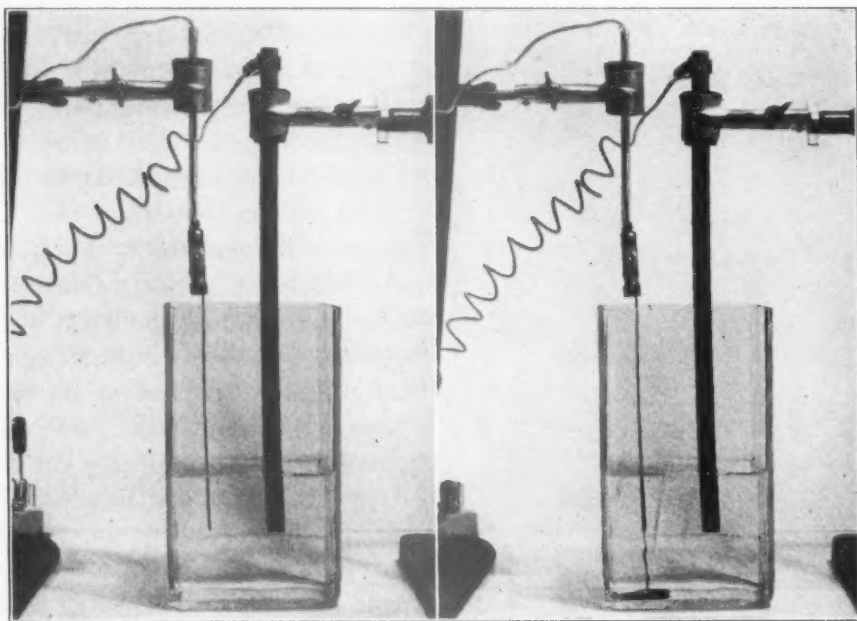


FIG. 4.

FIG. 5.

FIGS. 4 AND 5.—ELECTROLYTIC CELL TO DEMONSTRATE HIGH DENSITY OF CORROSION PRODUCTS.

Fig. 4, circuit open; Fig. 5, circuit closed.

steel specimen clamped at a slight angle to the vertical; so that the stream is always in contact with the steel specimen. The flow of the stream should correspond to about six drops per minute. The difference in index of refraction of the stream makes it easy to follow its course when it is illuminated along the plane of the metal specimen. The heavy ferrous chloride flows to the bottom of the beaker with little diffusion upward during the length of the run, which in all the experiments was 4 hr. A visible groove forms under the stream in a time as short as 10 or 15 min. The action is rapid and verifies the extreme activity of the cell previously postulated.

The ferrous chloride stream of concentration sufficiently greater than the beaker solution to produce downward flow corresponds to the contents



of the natural pit. Naturally formed corrosion products must also be heavier than the surrounding corrodent to produce the grooves mentioned earlier. Their density difference can be satisfactorily demonstrated by producing corrosion of 18-8 in sodium chloride using an external source of current. The experiment is pictured in Fig. 4. A graphite cathode and 18-8 wire anode, the anode corresponding to the pit surface, are immersed in 5 per cent NaCl. When the circuit is closed as in Fig. 5, a moderate current (0.3 amp.) produces corrosion of the anode and the corrosion products can be seen flowing from the electrode in a thin, sharply defined stream to the bottom of the vessel.

All evidence points to the fact that the electrolytic cells described above account in large part for the rapid corrosion of metal inside the pit.

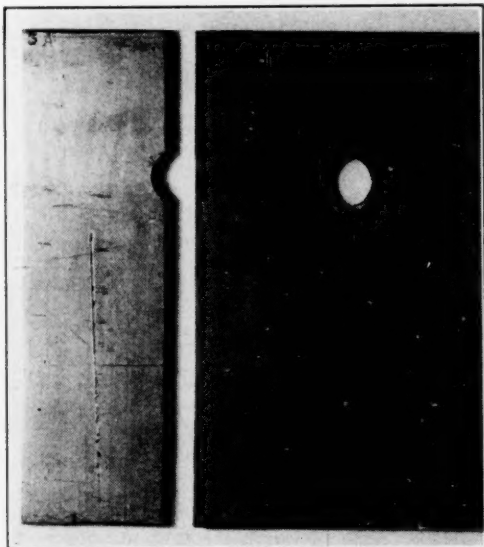


FIG. 6.—ELONGATED PIT PRODUCED BY STREAM-BEAKER EXPERIMENT (LEFT) AND BY SEA-WATER IMMERSION (RIGHT).

Fig. 6 represents two typical 18-8 specimens that exhibit the characteristic elongated pits. The specimen on the right was immersed in sea water at Boston Harbor for a period of one year. The pit began at the point of suspension (a bakelite rod through the hole) and progressed in the direction of gravity. A thin metal covering was originally in part over the groove. This was removed during subsequent probing for pits but has not altered the groove except to make it appear wider. The specimen on the left shows a similar groove produced

in 4 hr. in the stream-beaker experiment described above, in which 50 per cent  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  solution flowed into a 10 per cent  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  solution. Although the corroding agents and lengths of time of corrosion differed, the fundamental mechanism appears to be the same for either ferric chloride or sea water. Ferric chloride replacing dissolved oxygen of the sea water engenders a higher current and corrosion rate. In the pit one would expect approximately the same corrosion products, whether sea water or ferric chloride produced the corrosion.

It was interesting to observe, in subsequent stream-beaker experiments on all the 18-8 specimens (using a steel known in the trade as No. 1 finish), that no pits formed on either face of the specimens except under the stream, despite the fact that they were in contact with very corrosive ferric chloride. Apparently sufficient current flows because of rapid corrosion under the stream to protect cathodically the surface outside



the pit. It is important to note that the factors that serve to protect a large portion of the metal serve to accelerate corrosion at the focus; namely, the pit. The maintenance of passivity minimizes general solution but accentuates the possibility of high current densities at restricted areas.

Mild steel substituted for 18-8 in the stream-beaker experiment does not groove, although the general corrosion is very marked. Apparently in the absence of passivity the mild steel corrodes so rapidly in contact with ferric chloride that a blanket of ferrous chloride formed by the corrosion always exists between the solution and the metal. Hence, the potential between the stream and specimen is one of different concentrations of  $\text{Fe}^{++}$ . The potentials of concentration cells from theory and experiment are known to be very small compared with the potential of the active-passive metal cell. They are, therefore, unimportant potentials in the corrosion of steel subjected to a 4-hr. test. The high concentration of ferrous chloride in the stream serves, in fact, to slow down the solution of iron to ferrous ions and thus partially protects the metal under the stream. In some mild-steel specimens this protection is apparent.

The relative activity of ferrous chloride in establishing the active-passive metal cell suggested that other salts might also cause grooving. If this were so, any explanation of pitting action would find support in these experiments. Accordingly, several arrangements and combinations of both "stream" and "beaker" solutions were used to determine the extent of corrosion. The experiment was made semiquantitative by cleaning the specimens (2.5 by 12.5 by 0.32 cm.) uniformly in organic solvents, immersing to uniform depth in the beaker (7 cm.), allowing the stream to impinge 1 cm. below the surface of the beaker solution and controlling the rate of flow of the system to about six drops per minute. Weight loss for a 4-hr. run was then used as an index of the rate of corrosion. In Table 1, several stream-beaker experiments are listed, together with the corresponding weight losses. A single type and manufacture of 18-8 was used unless otherwise stated.

In experiments 1 and 2 the relative corroding capacities of ferrous chloride and ferric chloride alone are compared. In experiment 1 the corrosion process is simply a very slow general solution of the metal. The slight tarnishing under the stream is evidence that passivity has been broken down uniformly—not in local areas as in experiment 2, where ferric chloride was used. In our experience high concentrations of chlorides at low pH almost always destroy passivity and corrode the metal generally.

Ferric chloride in contact with stainless steel, and at not an extremely low pH, tends to keep the steel passive because of its oxidizing capacity, but at certain favored spots or pit foci reduction of the ferric chloride

takes place. Ferrous chloride is formed, which can destroy passivity, the active metal thereby establishing electrochemical cells with the passive metal and initiating pitting at these local areas. The areas surrounding the incipient pit, being cathodic, are protected against pitting or tarnish and hence retain their original reflectivity, thus differing from experiment 1, in which the surface of the steel in contact with ferrous chloride is tarnished.

TABLE 1.—*Stream-beaker Experiments*

Experiment	Stream Solution	pH	Beaker Solution	pH	Wt. Loss, Grams	Remarks
1	FeCl <sub>2</sub> ·4H <sub>2</sub> O, 60 per cent in 0.05N HCl	-0.13	Air		0.000	Stream path tarnished, no pitting.
2	FeCl <sub>3</sub> ·6H <sub>2</sub> O, 100 grams per liter 0.05N HCl	1.05	Air		0.005	Specimen pitted along edges of stream.
3	FeCl <sub>2</sub> ·4H <sub>2</sub> O, 60 per cent in 0.05N HCl	-0.13	FeCl <sub>3</sub> ·6H <sub>2</sub> O, 100 grams per liter, 0.05N HCl	1.05	0.192	Succession of pits under stream.
4	FeCl <sub>2</sub> ·4H <sub>2</sub> O, 60 per cent	1.38	NaCl, 1 molal	7.	0.001	Slight groove under stream.
5	FeCl <sub>2</sub> ·4H <sub>2</sub> O, 60 per cent in 0.05N HCl	-0.13	FeCl <sub>3</sub> ·6H <sub>2</sub> O, 100 grams per liter 0.05N HCl	1.05	1.32	General corrosion. No pitting or groove under stream.
6	FeCl <sub>2</sub> ·4H <sub>2</sub> O, 10 grams in 100 c.c. saturated NaCl	2.03	FeCl <sub>3</sub> ·6H <sub>2</sub> O, 100 grams per liter 0.05N HCl	1.05	0.120	Succession of pits under stream.
7	FeCl <sub>3</sub> ·6H <sub>2</sub> O, 10 grams in 100 c.c. saturated NaCl	1.05	FeCl <sub>2</sub> ·4H <sub>2</sub> O, 100 grams per liter 0.05N HCl	1.18	0.030	Succession of pits under stream. Tarnishing.
8	NaCl (saturated) approx. 6 molal	7.	NaCl (1 molal)	7.	0.000	No pitting or tarnishing.
9	NaCl (saturated)	7.	FeCl <sub>3</sub> ·6H <sub>2</sub> O, 100 grams per liter 0.05N HCl	1.05	0.153	Succession of pits under stream.
10	SnCl <sub>2</sub> ·2H <sub>2</sub> O, 20 per cent	0.98	SnCl <sub>4</sub> ·5H <sub>2</sub> O, 48 grams per liter	0.52	0.003	General staining. No pitting.
11	FeSO <sub>4</sub> ·7H <sub>2</sub> O, 50 per cent	2.56	FeNH <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O 0.37 molal in 0.05N H <sub>2</sub> SO <sub>4</sub>	1.29	0.000	No pitting or tarnishing.
12	FeCl <sub>2</sub> ·4H <sub>2</sub> O, 50 per cent	1.98	FeNH <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O, 10 per cent	1.75	0.075	Succession of pits under stream.
13	Fe(OOCCH <sub>3</sub> ) <sub>2</sub> 1.2 molal	2.42	Fe(OOCCH <sub>3</sub> ) <sub>2</sub> , 0.2 molal	2.05	0.001	Some tarnishing. No pitting.
14	FeSO <sub>4</sub> ·7H <sub>2</sub> O, 100 grams per liter 50 per cent H <sub>3</sub> PO <sub>4</sub>	-0.03	FeNH <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O, 10 per cent, 50 grams H <sub>3</sub> PO <sub>4</sub> per liter	0.56	0.000	No pitting or tarnishing.
15	Fe(NO <sub>3</sub> ) <sub>3</sub> , 50 per cent	-0.28	FeSO <sub>4</sub> ·7H <sub>2</sub> O, 100 grams per liter 0.05N H <sub>2</sub> SO <sub>4</sub>	1.90	0.000	No pitting or tarnishing.
16	FeCl <sub>2</sub> ·4H <sub>2</sub> O, 10 grams in 100 c.c. saturated NaNO <sub>3</sub>	1.99	FeCl <sub>3</sub> ·6H <sub>2</sub> O, 10 grams in 100 c.c. 5 per cent NaNO <sub>3</sub>	1.28	0.000	No pitting or tarnishing.

Although ferrous chloride flowing in a stream over 18-8 in air corrodes the specimen very little, the same ferrous chloride flowing over the specimen immersed in ferric chloride corrodes the specimen very much more. In experiment 3, this arrangement generates the high electric currents previously discussed, with resultant high weight loss. Such high

currents serve to dissolve metal rapidly under the stream, forming a succession of pits or a groove. At the cathode areas in contact with ferric chloride,  $\text{Fe}^{+++}$  ions absorb electrons to form  $\text{Fe}^{++}$ , which can diffuse away from the steel surface before the concentration becomes sufficient to destroy passivity. Ferric chloride, as previously stated, acts as a depolarizer and also serves to maintain passivity of metal surrounding the pit.

In naturally corroding systems, oxygen is the usual depolarizer. In experiment 4, this depolarizer is present dissolved in sodium chloride into which ferrous chloride flows. A definite groove is formed, but it represents a small amount of corrosion compared with experiment 3. Without oxygen, the electrolytic process depends on the rate at which hydrogen can be released. This process is slow and only for nonoxidizing, highly ionized acids like hydrochloric does the reaction proceed at a significant rate.

The active-passive metal corrosion cell is characteristic of all passive metals and alloys and also of normally active metals made passive, like iron immersed in chromates. On nonpassive metals, all the surface is initially active and with appreciable corrosion tendency; so that corrosion is much more uniform but weight losses are higher. This is noted in experiment 5. An appreciable concentration of ferrous chloride is always in immediate contact with the specimen formed by fairly rapid reduction of ferric chloride in which it is immersed. Potential differences between stream and beaker solutions are small, therefore no groove forms under the stream.

In experiment 6, the stream solution is ferrous chloride, in experiment 7, ferric chloride, both dissolved in saturated sodium chloride. The one experiment is the reverse cell of the other. Offhand, according to theory, one would expect that when ferric chloride flows into ferrous chloride, because of the direction of current flow, pitting would take place anywhere but under the stream. Actually the current flow tends to retard corrosion, for the weight loss is one-fourth that of the ferrous chloride into ferric chloride cell. Pitting takes place under both streams, however, probably because inherent in the very corrosive nature of ferric chloride in concentrated sodium chloride, local cells of the metal under the stream operate despite the current that flows from induced cathode to anode areas. Metal in contact with ferrous chloride solution of the beaker dissolves generally, so that some tarnish is observed.

The relative unimportance of concentration cells in accounting for continuation of corrosion is seen in experiment 8. The potential difference set up between saturated sodium chloride (6N) and less concentrated sodium chloride (1N), is too small to have any effect on the specimen in 4 hr. The experiment was varied by running dilute sodium chloride in the stream weighted with sugar; and with concentrated

sodium chloride in the beaker. The result was similar—no corrosion or tarnishing.

In experiment 9, concentrated sodium chloride flows into ferric chloride. Were acidity or low pH of the corroding solution essential to rapid corrosion, no groove or pitting would have formed. Actually, considerable weight loss was observed, with accompanying grooving and pitting. Later, experiments are described in which the stream solutions were definitely acid, but in which the specimens showed no corrosion. Evidently the pH of the stream solution is not a critical factor.

Experiment 10 illustrates the effect of another oxidation-reduction system,  $\text{Sn}^{++++}$ ,  $\text{Sn}^{++}$ . In this instance, some general corrosion but no pitting takes place. The general corrosion is probably caused by the hydrochloric acid formed by hydrolysis. The reason that no pitting takes place lies apparently in the low oxidizing capacity of stannic chloride solutions, so that passivity of the alloy is not maintained. The molal electrode potential of the stannic-stannous system as given in the literature is only  $-0.15$  volt, whereas for the ferric-ferrous system the value is  $-0.77$  volt. By way of comparison, the value determined for the concentration cell of experiment 8 is approximately  $-0.1$  volt.

In experiments 11, 12, 13, 14 and 15, the relative importance of the chloride ion in any rapid corrosion process of 18-8 is apparent. Sulphate, acetate, nitrate and phosphate ions when in combination with ferrous and ferric ions have little effect on the steel specimens in 4 hr. All the "stream" and "beaker" solutions are relatively high in acidity, so that acidity itself is not a unique factor. The substitution of ferrous chloride for ferrous sulphate in experiment 12, however, produces severe pitting.

In experiment 16, the presence of nitrate ions, unlike sulphate, acetate, and phosphate ions, renders ineffective the ferric-ferrous chloride cell. Nitrates appear to act as inhibitors in which the usual action of ferrous chloride in breaking down passivity is prevented. We found that nitrates in sufficient concentration in ferric chloride solutions entirely prevent pitting of stainless steels and reduce the general corrosion to a minimum. Ordinarily a specimen of 18-8 measuring 5 by 1 by  $\frac{1}{8}$  in., immersed in 10 per cent  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , pits and corrodes severely in a few hours (0.26 grams loss in 4 hr.). In a period of two years and three months, we found that a similar specimen, immersed in 10 per cent  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  containing 3 grams  $\text{NaNO}_3$  per 100 c.c. of solution lost only 0.0013 grams and showed no evidence whatever of pitting.

From these experiments, in the absence of nitrates, presumably at least two factors are involved in the rapid corrosion of 18-8, one being a sufficient oxidizing potential, the second a sufficient concentration of chloride ions. The factor of a sufficiently high oxidizing potential was made more plausible by a series of immersion tests in various reagents,



some of which were capable of forming solutions of the same metal of differing valences and hence could form oxidation-reduction systems, and others that could not. The specimens, measuring 2.5 by 12.5 by 0.32 cm., were immersed in solutions of approximately 0.5 molality for 24 hr. and presence of pits was recorded. It should be noted that any deviation from this concentration affects only slightly the operating potential, approximated by the molal potential. In Table 2 are listed the solutions and the standard oxidation-reduction potentials as given in the literature. Pitting takes place in the solutions whose molal oxidation potential is more negative than  $-0.15$  volts.

In addition to the examples given, it has already been pointed out that salt solutions, like sea water containing dissolved oxygen, pit stainless steels. The potentials operating are also more negative than  $-0.15$  volt. The molal electrode potential for oxygen in acid solutions ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$ ) is  $-1.23$  volt, and in alkaline solutions ( $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4e^-$ ),  $-0.40$  volt. Certain additional metal-oxidizing salts pit stainless steels.  $\frac{1}{2}$  M  $\text{TiCl}_3$  and  $\frac{1}{2}$  M  $\text{Ce}(\text{SO}_4)_2$ , the latter containing chloride ions, are also effective, although the pitting is

TABLE 2.—*Solutions and Oxidation Reduction Potentials*

Solution	$E_0$ (Molal Oxidation-reduction Potential), Volts	Presence of Pits
$\text{FeCl}_3$ .....	$-0.77$	+
$\text{CuCl}_2(\text{CuCl} \rightarrow \text{Cl}^- + \text{Cu}^{++})$ .....	$-0.57$	+
$\text{SnCl}_4$ .....	$-0.15$	—
$\text{NiCl}_2$ (no lower valence salt).....	$0.00$	—
$\text{MnCl}_2$ (no lower valence salt).....	$0.00$	—
$\text{TiCl}_4$ in 0.5N HCl.....	$-0.04$	—
$\text{CrCl}_3$ .....	$+0.4$	—

less than for ferric chloride and the addition of some hydrochloric acid is necessary. The actual operating potentials are not known definitely for these salts, because of the complications of hydrolysis, complex formation and insoluble lower-valence chlorides formed in the corrosion process, but the pronounced negative molal electrode potentials for the metal oxidation-reduction systems indicate by comparison negative values below  $-0.15$  volts. As is true for cuprous chloride, insoluble lower-valence chlorides for these salts adhere to the immersed steel surface so that the potential probably involves formation of the lower-valence chloride. For thallium involving insoluble thallium chloride, the potential ( $\text{TlCl} \rightarrow \text{Tl}^{+++} + \text{Cl}^- + 2e^-$ ) is  $-1.36$  volts.

It appears to be general, therefore, that only the solutions capable of forming systems of appreciable negative oxidation-reduction potentials ( $E_0 < -0.15$  volt) pit stainless steels. For other types of solutions,



corrosion is by uniform solution of the surface. Solutions like nickel chloride, which ordinarily form no lower-valence salts, tend to corrode the specimens more rapidly than alkali salt solutions because of their acidic character due to hydrolysis. They act much like dilute solutions of hydrochloric acid, which attack 18-8 generally through their ability to destroy passivity. If oxygen concentration in these solutions is sufficiently high and hydrogen-ion concentration sufficiently low so that hydrogen liberated is entirely oxidized and oxygen is in contact with the steel surface, any corrosion would then be expected to take place by pitting, as occurs in aerated salt solutions like sea water.

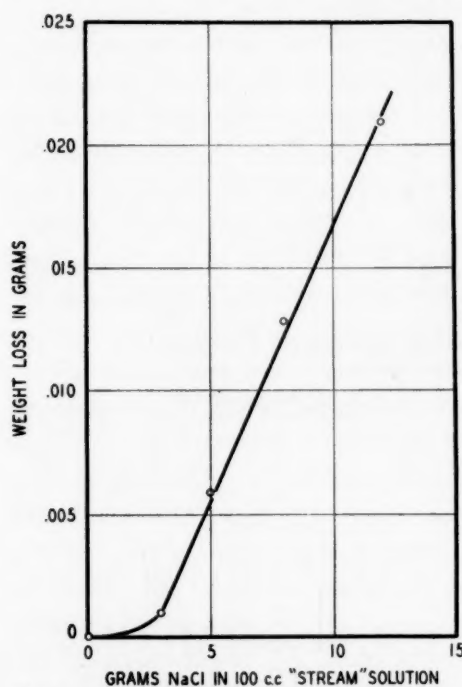


FIG. 7.—EFFECT OF CHLORIDE-ION CONCENTRATION ON PITTING RATE.

ing, as occurs in aerated salt solutions like sea water.

The effect of chloride ion in producing serious pit corrosion has been recognized in practice for a long time. The stream-beaker experiment made it possible to measure quantitatively in a simple way the effect of its ion concentration on pit formation. A series of experiments was run in which the chloride-ion concentration was increased in steps in the stream solution, keeping the pH identical. The ferrous-feric system was used to produce the potential difference necessary to start and continue corrosion. The stream solutions, in addition to varying amounts of sodium chloride, contained uniformly for all solutions: ferrous sulphate (10 grams  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  per 100 c.c. solution) acting partly as buffer, and

sucrose (15 grams sucrose per 100 c.c. solution), the latter being an inert addition to give the solution additional specific gravity. Because the addition of sodium chloride to ferrous chloride solutions was found to decrease their pH, the pH of each solution was adjusted by adding sulphuric acid. The pH of the stream solution containing 12 grams sodium chloride per 100 c.c. solution was 2.9; other solutions containing less sodium chloride were adjusted to this value, the addition of acid necessary being very little. The beaker solutions were all 0.37 molal ferric ammonium sulphate ( $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ) (same concentration of  $\text{Fe}^{+++}$  as 10 per cent  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 0.05 molal  $\text{H}_2\text{SO}_4$ ). The specimen, run with no chloride ion in the stream, lost no weight in the 4-hr. period; the specimen in which the stream contained 12 grams NaCl per 100 c.c. lost 0.021 gram. The weight losses for all the runs are plotted in Fig. 7,

in which the sodium chloride concentration in the stream is plotted as abscissa, the weight loss of the specimen, which was due almost entirely to pitting, as ordinate. The plot shows that the addition of chloride ion to sulphate solutions at constant pH increases the rate of corrosion considerably. The rate of corrosion between 3 grams and 12 grams NaCl per 100 c.c. solution is found to be linear with concentration.

### THE ARTIFICIAL PIT

The effect of concentration of chloride ion on rate of corrosion has a particular bearing on the mechanism of the pitting phenomenon, since it can be shown that chloride ions tend to concentrate in areas undergoing corrosion and thereby accelerate the corrosion process. Because chloride ion is a relatively small ion with high mobility, in any electrochemical process it carries a greater proportion of the electric current per ion than any other common ion, except  $H^+$  or  $OH^-$ . In any corrosion process involving flow of electric current through ferric or sodium chloride, the chloride ions would carry more current than sodium ions or ferric ions. The greater current-carrying capacity of chloride ions is one of the factors that make them so effective as corrodents. Higher current densities build up, which account for a high corrosion rate. In addition, the chloride ion rapidly migrates toward the anodes or pits, accumulating there and in higher concentration stimulating the corrosion rate as shown by Fig. 7.

The natural accumulation of chloride ion at the anode was demonstrated by constructing a cell to simulate the natural pit. This cell was constructed of a porous cup containing a piece of 18-8 pipe, stoppered at the bottom, for use as an anode. Its diameter was only slightly less than that of the cup, which permitted a small volume of anolyte. A graphite electrode as cathode was placed outside the cup as depicted in Fig. 8. The electrolyte was 5 per cent NaCl and a current of 0.5 amp. from a storage battery was accurately maintained through the cell for 2 hr. Analyses were made on the anolyte, this corresponding to the corrosion products of the pit, as the electrolysis proceeded. The anode current density was 0.0215 amp. per sq. cm., approximately that which,

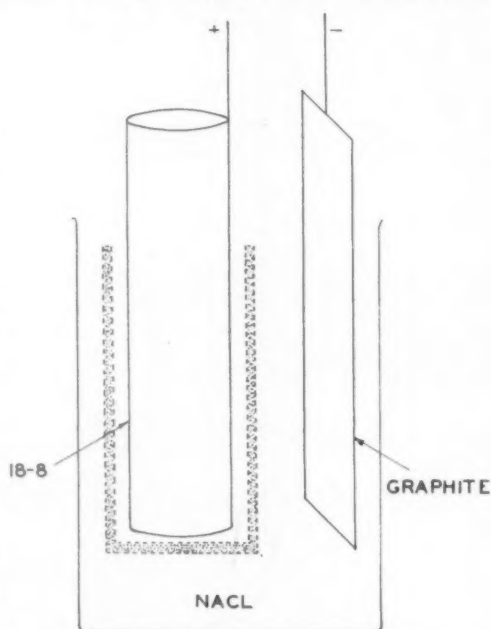


FIG. 8.—ELECTROLYTIC CELL TO SIMULATE REACTIONS WITHIN PIT.

according to the electrochemical theory, is calculated to accompany the formation of pits in accelerated tests using 10 per cent ferric chloride. Hydrogen gas was evolved at the graphite cathode, and corrosion products, but with no attendant gas evolution, accumulated in the porous cup, where they could be sampled from time to time for analysis.

After the run, the anode was found to have pitted generally over the entire surface. Analysis showed that all the constituents of the steel had dissolved in the same proportions as they exist in the steel. The weight loss of the anode in a 2-hr. run corresponded with the equivalent weight of the corrosion products within the experimental error. This

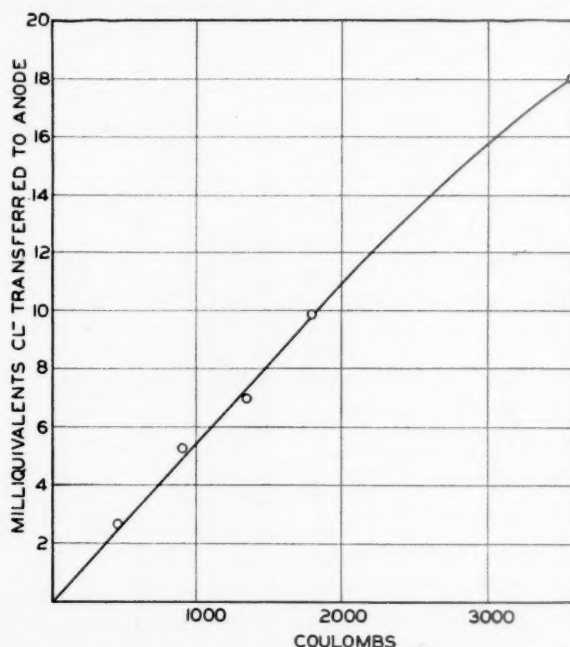


FIG. 9.—TRANSFERENCE OF CHLORIDE IONS TO ANODE ON PASSAGE OF CURRENT.

indicated that probably there were no insoluble reaction products retained by the cavities or pits of the anode. The corrosion products were found by analysis to consist of ferrous, chromic and nickel chlorides. On this basis, the current efficiency was calculated to be 99 per cent. In the course of this experiment, we observed the very interesting phenomenon that ferric ions dissolved from the anode during the very first moments that the current was turned on, but that ferric ions soon disappeared and ferrous ions alone were thereafter present in the corrosion products. This is a property of passive stainless steels whose proposed explanation is contained in a previous paper.<sup>4</sup>

In accordance with prediction, chloride ion accumulated in the porous cup and diminished in concentration outside. A plot of the transference of chloride ion with coulombs passed through the cell is shown in Fig. 9. With a small volume of solution in contact with the anode, which is the

condition in the natural pit, this transference can result in a very appreciable increase of chloride-ion concentration at the focus of corrosion.

At the same time that the chloride-ion concentrations were determined, pH measurements showed that the solution surrounding the anode rapidly became acid and that surrounding the cathode rapidly became alkaline. The acidity in this case undoubtedly is due to hydrolyzed metal chlorides formed at the anode and the alkalinity to formation of sodium hydroxide. The pH of the anolyte appears to approach with time a steady value, which is approximately that of saturated ferrous

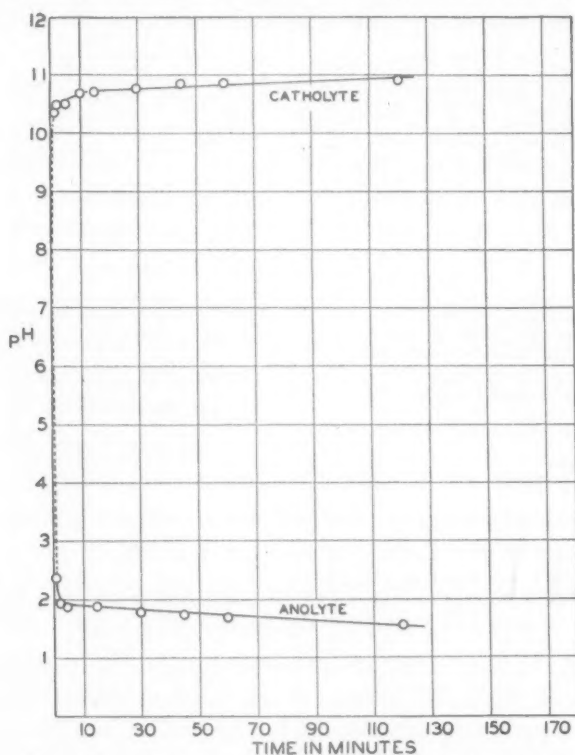


FIG. 10.—pH CHANGES ON PASSAGE OF CURRENT.

chloride. The trend of pH is shown in Fig. 10, in which time of electrolysis is plotted as abscissa.

The above-described model of a pit demonstrates therefore that chloride ion accumulates at the seat of corrosion, this accumulation having been shown to accelerate corrosion. Furthermore, at the pit, acid solutions are present, even though the external solution may be neutral or alkaline.

#### CONTACT CORROSION

Any condition that permits the formation and accumulation of corrosion products in oxygen-containing solutions like sea water would be expected from what has preceded to initiate rapid corrosion at the areas where such accumulation occurs. In solutions of other depolarizers



than oxygen, rapid corrosion processes to form pits could also take place except in those of relatively positive oxidation-reduction potentials, in which case corrosion would be by general solution. Accumulation of corrosion products can readily take place whenever areas of metals immersed in corroding solutions are shielded from oxygen, or oxidant acting as depolarizer, by contact with other metal or nonmetal. The resulting corrosion, which invariably takes place at the areas of contact, is known as contact corrosion.

The action can be illustrated by Fig. 11. At *B* the electrolyte is relatively less free to move and circulate than at *A*. Consequently, if some oxygen is used up at *A* and *B* by slight general corrosion, which takes place in all instances for all metals, the area at *B* would become exhausted of oxygen before *A* and in addition corrosion products would accumulate to higher concentrations at *B*. The differences in oxygen concentration at *A* and *B* would initially give rise to an oxygen concentration cell with anode at *B* and cathode at *A*. Corrosion currents from this source, small in magnitude, would account for some small accumulation of corrosion products at *B*.

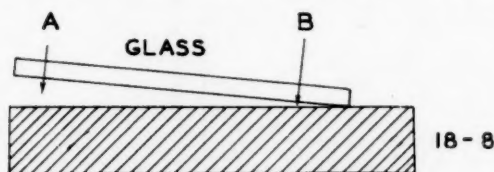


FIG. 11.—GLASS CONTACT SURFACE ON 18-8.

In addition, there is evidence that lack of oxygen at *B* may produce active alloy even before any noticeable concentration of corrosion products accumulates in the neighboring electrolyte. This was demonstrated by measuring the potentials of 18-8 electrodes immersed in oxygen-free 4 per cent NaCl solution. The potentials initially noble became active with time, gradually leveling off to a steady potential several tenths of a volt more active than initially. During this time, the pH of the sodium chloride remained constant and corrosion products, if present, could not be detected chemically. In aerated 4 per cent NaCl, on the other hand, potential data showed that 18-8 tends to become more passive with time. Potential data for two typical 18-8 electrodes measured against the saturated calomel cell are plotted in Fig. 12; referring to Fig. 11, area of metal at *B* is comparable with the former electrode, the area at *A* with the latter.

The corrosion cell established between active and passive areas of alloy gives rise to corrosion currents higher in magnitude than the oxygen concentration cell and determines rapid corrosion at the area of contact, the rate depending on rate of depolarization over the large cathode area. Because of high current densities, which protect the surrounding cathodic areas, the corrosion still further concentrates at the anode without spreading, the final result being a deep pit.

Such contact corrosion, caused, for example, by dirt accumulating on the steel surface, or attachment of barnacles in sea-water installations,



obviously can be avoided by removing the contact substance. Hence the advisability of keeping 18-8 surfaces polished and free of surface film. It is also obvious that stainless steel in contact with well aerated solutions or rapidly moving solutions is less subject to contact corrosion because of the better uniform aeration and consequent passivity of all parts of the steel surface. Stagnant solutions, on the other hand, are particularly liable to cause pitting because of the possibility of oxygen-depleted volumes of solution in contact with the alloy. Most solutions in contact with stainless steels should, therefore, be aerated if corrosion is to be minimized. From the standpoint of the alloy, it follows from this theory

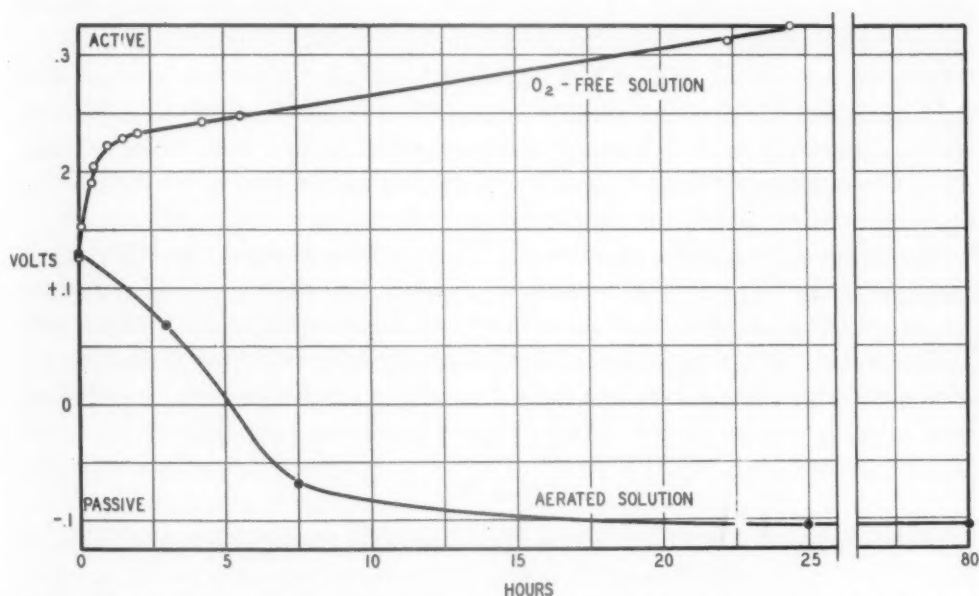


FIG. 12.—TIME-POTENTIAL MEASUREMENTS IN 4 PER CENT SODIUM CHLORIDE VS. SATURATED CALOMEL CELL, 18-8 ELECTRODE, PICKLED.

that contact corrosion could be diminished by altering composition and treatment of the alloy to reduce general corrosion. Corrosion products would then less readily accumulate. It should be noted that contact corrosion could also be minimized by proceeding in the opposite direction; that is, by increasing the general corrosion of the alloy. This, however, produces an alloy not passive, whose average corrosion rate would be much higher than that of passive stainless steels.

#### FACTORS THAT INDUCE PITTING

A study of the nature of pit foci constitutes a broad field of investigation in itself, yet the theory of pit growth outlined in the foregoing pages, plus some preliminary experimental work, suggests plausible explanation for differences in numbers of pit foci existing in certain steels. Iron sulphides, for example, are readily attacked in acid chloride solutions to form

ferrous chloride. These sulphides occurring in stainless steel as inclusions would therefore be expected to cause greater corrosion and pitting than in sulphur-free steels, because of the possibility of ferrous chloride filling the cavities originally occupied by metallic sulphides. This is also true of selenium-bearing stainless steel. Ferric chloride tests show that an 18-9 steel containing 0.2 per cent Se corrodes over 20 times as much as a selenium-free chromium-nickel steel of the same composition.

Inclusions or segregations on the surface of stainless steel that can set up galvanic cells with the surrounding metal would also be expected to accelerate corrosion. Galvanic action would generate soluble metal chlorides in the vicinity of the inclusion or segregation, which would destroy passivity of a limited area of metal in contact, eventually establishing a corrosion cell of active-passive metal. Only inclusions and segregations that are electrically conducting would accelerate corrosion by this mechanism. The metal oxides and silicates responsible in large part for so-called "dirty steels" are known to be nonconductors. In agreement dirty steels are stated to corrode no more than other steels.<sup>6</sup>

Surfaces of stainless steels with cracks and fissures would permit accumulation of corrosion products formed by slow general solution, therefore these steels should have lower corrosion resistance. The detrimental effect of cracks and fissures has already been pointed out by J. Wulff.<sup>7</sup> In addition, it has been known for some time that a polished steel with flowed surface shows increased corrosion resistance.

#### SUMMARY

Pit corrosion of stainless steels appears to be caused by breakdown of passivity at localized areas through electrolytic action. Potential differences on the surface give rise to corrosion products at the focus of corrosion. These potential differences may be established, for example, by certain kinds of inclusions or segregations in the alloy or by differences in oxygen or oxidizing concentration of the electrolyte in contact (contact corrosion). The corrosion products, largely ferrous salts, acidic in character (pH 1.4 to 2.0), have the property of destroying passivity and establishing a corrosion cell between passive and active metal, the operating potential difference being about 0.5 volt. Current then flows in greater magnitude with accelerated formation of corrosion products. If the corrosion products can accumulate, as in a pore or fissure of the metal surface, the high potential difference of the cell is maintained and pitting results. The rate of corrosion depends on the efficiency of depolarization at the cathodic areas surrounding the anodes or pits. Because of the noncorrosive character of metal outside the pit, further protected by corrosion currents that limit access of negative ions to cathodic metal, the incipient corroded area is limited in surface dimensions and tends to grow deep rather than broad.

Two factors appear essential for the rapid pitting of 18-8 stainless steel; the one being a sufficient concentration of chloride ion, and the other a sufficient oxidizing potential of the corroding solution. If the molal oxidation-reduction potential of the corroding solution is more positive than approximately  $-0.15$  volt, 18-8 loses passivity and tends to corrode by general solution rather than by pitting. Only in solutions that normally maintain passivity, and in which 18-8 is therefore corrosion-resistant in the usual sense, is pitting apt to occur. For oxygen dissolved in salt solutions, the molal potential is  $-0.40$  to  $-1.23$  volt, hence these solutions as observed maintain passivity and in these solutions pitting can occur.

The observation that growth of pits is in the direction of gravity, forming "streamers," is explained by the action of heavy corrosion products of the pit in leaking out to contact new areas of passive alloy. Wherever such contact is made, passivity is destroyed and new corrosion cells are established, which become an elongation of the original.

If corrosion products do not accumulate, oxygen or oxidizing solution diffusing to the attacked area will tend to reform the passive state and prevent pit growth. Hence pitting is less in well aerated and stirred solutions.

18-8 may be activated by acids or acid chlorides to such a degree that passivity is not regained by contact with oxygen in salt solutions. In this case corrosion already initiated is not inhibited by aeration. The alloy is passivated, however, if dried in air or washed with distilled water containing dissolved oxygen.

All these statements of theory and observation are based on laboratory experiments and on service tests in sea water. The "stream-beaker" experiments in which synthetic corrosion products flowed in a stream over metal immersed in a corrodent demonstrated the action of corrosion products in the mechanism of the elongated pit, the importance of the passive-active surface cell in the mechanism of pitting and the effect of chloride-ion concentration in the stream in increasing the rate of pitting. The artificial pit in which 18-8 alloy was made anode in a sodium chloride electrolytic cell supplied information on the nature of the corrosion products and the mechanism of corrosion inside the pit. Electrochemical potential measurements indicated that corrosion products break down passivity, as does lack of oxygen in a salt solution in which 18-8 is immersed. The active to passive state transformation was found dependent not only on oxygen or oxidant concentration but also on sodium chloride concentration of the corrodent.

The mechanism of pit development, whether the corrodent is ferric chloride or sodium chloride, appears the same. Ferric chloride corrodes the alloy more rapidly than sodium chloride because it more rapidly depolarizes the cathodic areas.

Factors that possibly can account for initiation of pits are briefly reviewed in light of the accumulated evidence.

#### ACKNOWLEDGMENT

Throughout the investigation of which the results are outlined in this paper, the author was in close association with members of the Corrosion Committee at The Massachusetts Institute of Technology appointed to supervise the research concerning the pitting of stainless steels for The Chemical Foundation. For the advice and support given by Prof. R. S. Williams, Chairman, and by other members of the Committee, the author expresses his appreciation.

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#### DISCUSSION

(J. Hunter Nead presiding)

S. W. SHEPARD,\* Bound Brook, N. J.—I was impressed by Dr. Uhlig's evidence of the influence of gravity on the pitting of stainless steels. A corollary to this law might be that, all other things being equal, pits in a stainless-steel vessel will penetrate most rapidly in surfaces normal to the direction of the gravitational force. In other words, the bottoms of unstirred tanks and reaction vessels would tend to be penetrated at a more rapid rate than the sides. This is contrary to our experience. For instance, in unstirred tanks, the most rapid rates of pit penetration have consistently been on the side walls. However, "all other things" might not have been as equal as they seemed.

H. H. UHLIG (author's reply).—The fact that stainless-steel vessels fail on the sides more than on the bottom is not contrary to the observation that heavy corrosion products stimulate growth of pits in the direction of gravity. Mr. Shepard has pointed out that in vessels so corroded other things might not be equal, which would explain the corrosion he mentions. Were all things equal—for example, equal density of pit foci on sides and bottom—it would be expected that penetration of the bottom would occur first. If the sides were welded, however, or cold-worked by drawing and bending operations, the sides might inherently show greater tendency to pit than the bottom. In this case, the sides would be penetrated more rapidly than the bottom because of the earlier appearance of pitting at the sides.

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\* Metallurgist, Calco Chemical Division, American Cyanamid Co.



## Effects of Low-temperature Heat-treatment on Elastic Properties of Cold-rolled Austenitic Stainless Steels

BY RUSSELL FRANKS,\* MEMBER, AND W. O. BINDER\*

(New York Meeting, February 1940)

IN recent years a considerable tonnage of the 18 per cent chromium and 8 per cent nickel steels has been used in lightweight high-strength structures that must be resistant to deterioration under atmospheric conditions. These steels are austenitic in character and their strength can best be increased by cold-working. Although a marked increase in tensile strength is obtained, claims have been made that the cold-worked steels do not possess fully satisfactory elastic properties. Under certain conditions, however, this has caused no great concern, because, as explained by Ragsdale,<sup>1,2</sup> the cold-rolled steels have been widely applied for construction of lightweight, high-strength trains using spot welding for joining purposes. Ffield<sup>3</sup> agrees that the ease with which thin sections of the cold-rolled 18-8 steels can be joined by spot welding is greatly in their favor, but that they would be more satisfactory if higher elastic properties and a higher modulus of elasticity could be obtained. He states that, as far as the mechanical properties are concerned, the straight chromium stainless steel is superior to the cold-worked 18-8 steel, and in order to illustrate, he presented the data of Fig. 1, which also give a stress-strain curve for a low-carbon 13 per cent Cr steel. Ffield<sup>†</sup> proposed that columbium-bearing or titanium-bearing cold-rolled 18-8 steels be given a heat-treatment (preferably for 1 hr.) in the range 400° to 600°C. to precipitate carbides in order to obtain better mechanical properties.

Discussions by Sutton,<sup>4,5</sup> de Ganahl,<sup>6,7,8</sup> Krivobok and Lincoln,<sup>9</sup> Knerr,<sup>10</sup> and Thaden<sup>11</sup> have given further information on the properties of the cold-rolled 18-8 steels compared with other materials used in lightweight, high-strength structures. These investigators and others point out that the ultimate tensile strength of the cold-rolled 18-8 steel can be increased to 200,000 lb. per sq. in. or higher; Krivobok et al. indicate that

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Manuscript received at the office of the Institute Dec. 1, 1939. Issued as T.P. 1183 in METALS TECHNOLOGY, August 1940.

\* Union Carbide and Carbon Research Laboratories, Inc., Niagara Falls, N. Y.

<sup>1</sup> References are at the end of the paper.

<sup>†</sup> U. S. Patents 2080367 and 2080368.



best results in regard to ductility and strength are obtainable with steels containing from 17 to 18 per cent Cr, about 7 per cent Ni, and 0.10 per cent C. In all these discussions the chief point concerns the elastic properties of the cold-rolled steels. Neither Sutton nor Thaden agree that the cold-rolled steels have a low modulus in the elastic range. Thaden states that, in the purely elastic range, stainless steel, like ordinary carbon steel, has a Young's modulus of 28,000,000 to 29,000,000 lb. per sq. in., and that this holds not only for annealed but for cold-worked material. Sutton gives a long discussion on elastic characteristics and states that while the cold-rolled 18-8 steel offers no advantage for long columns, it is especially suitable for short-column construction. His

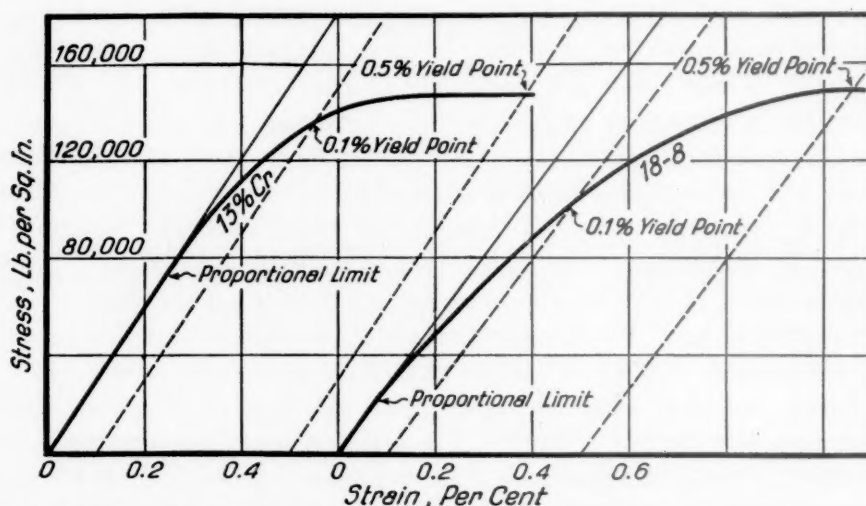


FIG. 1.—STRESS-STRAIN DIAGRAMS FOR HEAT-TREATED 13 PER CENT CHROMIUM STEEL CONTAINING 0.16 PER CENT CARBON AND FOR COLD-WORKED 18-8 STEEL CONTAINING 0.12 PER CENT CARBON. (*F<sub>field</sub>*.<sup>3</sup>)

opinion is that in order to compete with other materials the steels should exhibit an ultimate strength of 160,000 lb. per sq. in., a yield strength of 106,000 lb. per sq. in. and a proportional limit of 77,000 lb. per sq. in.

Studies have been made at the Union Carbide and Carbon Research Laboratories during the past few years on the elastic properties of the 18 per cent Cr, 8 per cent Ni steels both in the annealed and cold-rolled conditions and these investigations have extended to other types of austenitic corrosion-resisting steels. The investigation has related primarily to simple tests in tension. Some of the samples have been tested with the direction of rolling, and others across the direction of rolling. Soon after the investigation was started it was decided to secure the basic information on 18-8 steel sections large enough to permit axial loading to be obtained as well as accurate extension readings.

A cold-worked bar  $\frac{1}{2}$  in. thick by  $\frac{3}{4}$  in. wide of steel containing 18.95 per cent Cr, 7.69 per cent Ni, and 0.07 per cent C, with normal percentages

of manganese and silicon, was used for tests. In conducting the first tests, two Huggenberger gauges attached to opposite sides of the sample to compensate for bending were used to measure the strain during application of load. The deflection of each instrument was recorded, and the average of the two readings was used to calculate the unit strain corresponding to the applied load. Each division on these instruments represented an extension of 0.000033 in., and readings were estimated to  $\frac{1}{10}$  division (0.0000033 in.). The samples tested had a reduced section diameter of 0.375 in. As explained later, two of the samples had a 2-cm. gauge length, while the others had a 2-in. gauge length. Gripping devices similar to those recommended by the American Society for Testing Materials were used in a 60,000-lb. Baldwin-Southwark hydraulic testing machine. Loads were applied to the samples, and sufficient time was allowed after the application of each increment of load to permit the strain to be accurately measured. Without removal of the gauges, loads were applied beyond the elastic range into the plastic range until a permanent set had been obtained. When this point was reached, the strain gauge was removed and the sample fractured. The data obtained on annealed and cold-worked sections of the previously described 18 per cent Cr, 8 per cent Ni steel are given in Table 1,\* and an illustration of how the proportional limit was determined is given in Fig. 2.

The data of Table 1 and Fig. 2 show that the proportional limit of the annealed 18-8 steel is 18,300 lb. per sq. in. (curve 1) with a tensile strength of 84,200 lb. per sq. in., and the modulus of elasticity is approximately 28,000,000 lb. per sq. in. The data further show that while the tensile strength of the 18-8 steel is raised by cold-work to 140,300 lb. per sq. in., the proportional limit is slightly lower, and the calculations of modulus of elasticity give values on the order of 25,000,000 to 26,000,000 lb. per sq. in. This means that after cold-working the steel elongates or slips even when low stresses are applied. While a definite explanation for this effect cannot be given, it is probable that the slip is due to internal stress, which causes the cold-worked metal to elongate under low stress. This gives the impression that the actual modulus of elasticity of the steel is reduced by the cold-work. It was realized that if internal stress was responsible for the difficulty it would have to be removed without reduction of corrosion resistance, strength, fatigue resistance, ductility, or toughness. It was decided that relief from this stress might be accomplished by proper application of heat, which would not scale the cold-rolled steel excessively or render it subject to intergranular corrosion.

Experiments were made in which samples of cold-rolled 18-8 steels were heated for different periods of time between 600° and 50°C. (1110° and 120°F.). Except for extremely short heating periods, the steels

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\* See note under Table 3.

suffered a loss of ductility and became subject to intergranular corrosion after treatment at temperatures between 600° and 400°C. (1110° and

TABLE 1.—Tests Corresponding to Fig. 2

Steel containing 18.95 per cent chromium, 7.69 per cent nickel and 0.07 per cent carbon. Samples tested 0.375 inch in diameter

PART A.<sup>a</sup>—PHYSICAL PROPERTIES OF STEEL IN ANNEALED AND COLD-ROLLED<sup>b</sup> CONDITIONS

	Curve 1. Gauge Length 2 Cm. Air-cooled from 1100°C. (2012°F.)	Curve 2. Gauge Length 2 Cm. As Cold-rolled	Curve 3. Gauge Length 2 In. As Cold-rolled
Proportional limit, lb. per sq. in. ....	18,300	13,000	13,000
Tensile strength, lb. per sq. in. ....	84,200	140,300	143,300
Elongation, per cent in 1½ in. ....	72	25	21

<sup>a</sup> See note at end of paper.

<sup>b</sup> Percentage of cold reduction unknown.

750°F.). Also, under these conditions the improvement in elastic properties was not always consistent, and invariably the metal became covered with an oxide that could not be removed without destroying the cold-

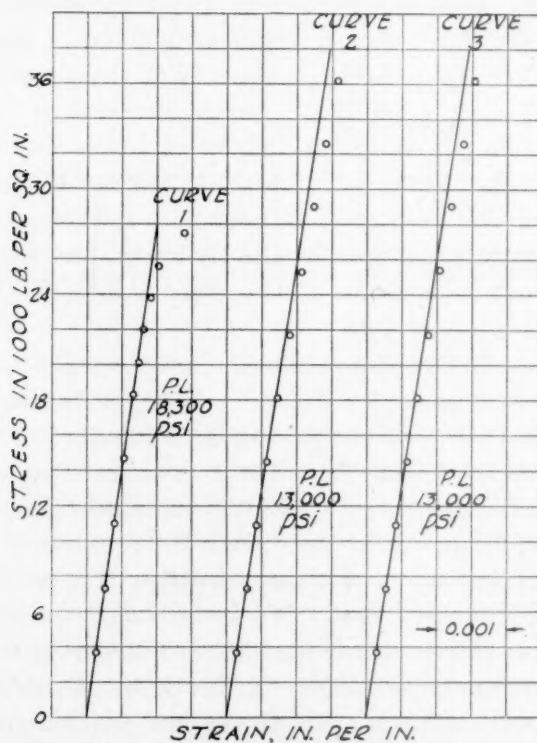


FIG. 2.—DETERMINATIONS OF PROPORTIONAL LIMIT FOR ANNEALED (CURVE 1) AND COLD-ROLLED (CURVES 2 AND 3) 18-8 STEEL DESCRIBED IN TABLE 1.

rolled surface. When the temperatures approached 300°C. (572°F.) the results were better but even these were not considered to be altogether

satisfactory, as in both ranges of temperature precipitation of carbides occurred, particularly during the long heating periods.

Different results were obtained on heating in the lower range between 300° and 100°C. (572° and 212°F.). Time was found to be especially important in bringing about uniform results in regard to elastic properties. The data showed that with short heating periods extending up to a matter of several hours, very little improvement in elastic properties was obtained, but when heating periods were extended to between 8 and 168 hr., for example at temperatures of about 200°C. (392°F.), a decided improvement in elastic properties took place. Uniform results were obtained at this temperature by using a period of 16 hr., while extending the heating period beyond 72 hr. produced no further improvement; in the discussion that follows these heating periods will be fully considered.

A tensile sample of the previously mentioned cold-worked 18-8 steel bar, of 0.375-in. dia., was heated to 200°C. (392°F.) and investigated for elastic properties according to the procedure used in securing the data on the annealed and as-cold-worked samples. In this experiment the cold-rolled sample prior to testing was held for 48 hr. at 200°C. (392°F.) and air-cooled. The data obtained are given in Table 2 and Fig. 3, together with those secured on a cold-rolled sample without the heat-treatment.

TABLE 2.—*Tests Corresponding to Fig. 3*

Steel containing 18.95 per cent chromium, 7.69 per cent nickel and 0.07 per cent carbon.

Samples tested 0.375 in. in diameter

PART A.<sup>a</sup>—PHYSICAL PROPERTIES OF STEEL IN COLD-ROLLED, AND COLD-ROLLED AND HEAT-TREATED CONDITIONS

	Curve 1. Gauge Length 2 In. as Cold-rolled	Curve 2. Gauge Length 2 In. Heated 48 Hr. at 200°C. (392°F.) and Air-cooled
Proportional limit, lb. per sq. in.....	13,000	31,000
Tensile strength, lb. per sq. in.....	143,300	145,800
Elongation, per cent in 1½ in.....	21	22.6

<sup>a</sup> See note at end of paper.

The data of Table 2 and Fig. 3 show that while the modulus of elasticity of the cold-worked 18-8 steel is 25,000,000 to 26,000,000 lb. per sq. in., this value is raised to about 28,000,000 lb. per sq. in. by heating at 200°C., which corresponds to the modulus of elasticity of the steel in the annealed condition. The data further show that the proportional limit of the cold-worked steel is increased from about 13,000 lb. per sq. in. to somewhat over 30,000 lb. per sq. in. by the heat-treatment at 200°C. Neither the tensile strength nor the percentage of elongation of the cold-worked steel changed appreciably, showing that these properties were not



materially affected even though the treatment produced an improvement in the elastic properties.

Another experiment was made to determine the effect of the heat-treatment on a pre-stressed sample. In this experiment a tensile sample 0.375 in. in diameter, of the same 18-8 steel bar ( $\frac{1}{2}$  in. thick by  $\frac{3}{4}$  in. wide), was tested in the as-cold-worked condition. The sample was stressed beyond the proportional limit to a total elongation of 0.0018 in. per in., and the elastic properties were measured during elongation. The

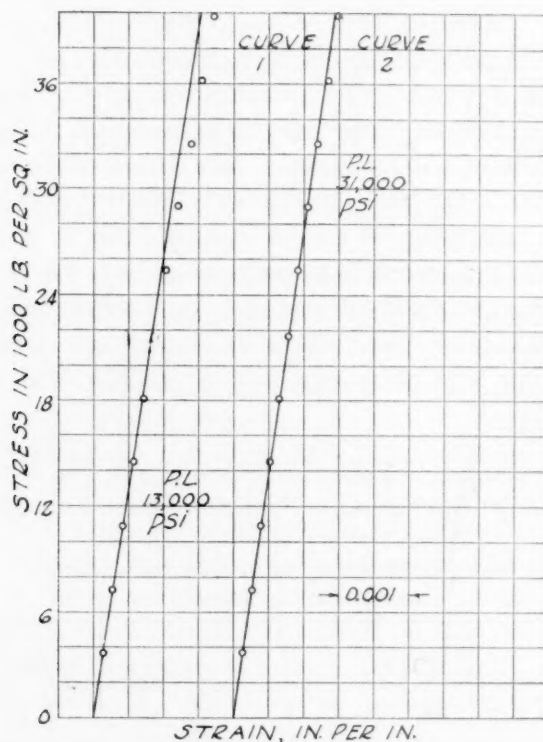


FIG. 3.—PROPORTIONAL-LIMIT DETERMINATIONS ON 18-8 STEEL DESCRIBED IN TABLE 2.

Curve 1. Cold-worked condition.

Curve 2. Cold-worked steel heated 48 hours at 200°C. and air-cooled.

load was then released and the sample was heated for 16 hr. at 200°C. (392°F.) and air-cooled. The sample was re-stressed, using, as in the previous tests, two Huggenberger gauges to measure the strain. The data obtained before and after the 16-hr. treatment at 200°C. are given in Table 3 and plotted on Fig. 4.

These data illustrate clearly the effect of heating at 200°C. (392°F.) on the elastic properties of the cold-rolled 18-8 steel, inasmuch as they were obtained on a single sample before and after heat-treatment. They show, as in previous tests, that the as-cold-rolled 18-8 steel has a modulus of elasticity of 25,000,000 to 26,000,000 lb. per sq. in., which, on heating as stated for 16 hr. at 200°C. (392°F.) is increased to approximately

28,000,000 lb. per sq. in. Also, the proportional limit is raised from 14,200 to 47,100 lb. per sq. inch.

The investigation was continued using a Berry gauge, which permitted readings to be taken over the standard 2-in. gauge length. Each division on this gauge represents an extension of 0.0002 in., and readings may be estimated to  $\frac{1}{10}$  division. In these experiments tensile samples were

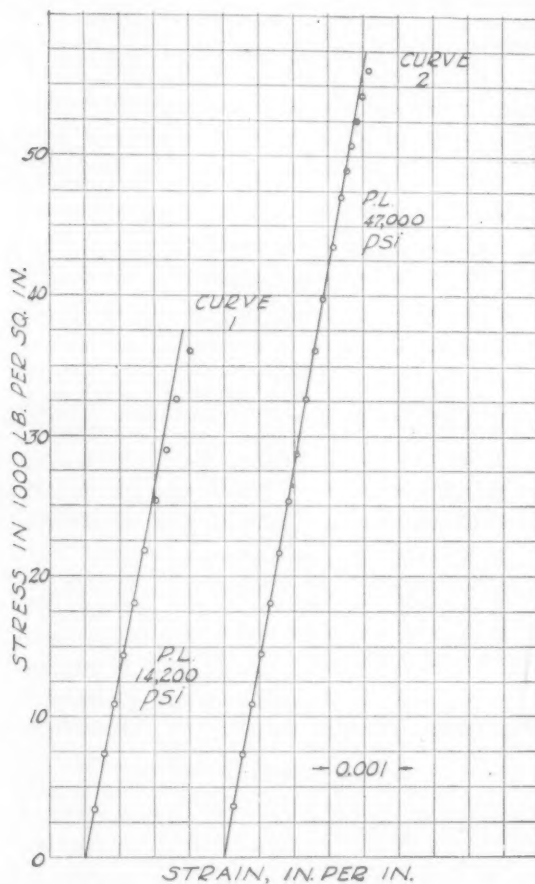


FIG. 4.—DETERMINATIONS OF PROPORTIONAL LIMIT ON 18-8 STEEL DESCRIBED IN TABLE 3.

Curve 1. As cold-rolled.

Curve 2. Same as cold-rolled sample stressed as shown by curve 1, then heated 16 hours at 200°C. (392°F.) and air-cooled.

taken from cold-rolled 18-8 steel strips that had been given different degrees of cold-work. The stress-strain measurements were extended sufficiently to determine the yield strength of the steel at 0.20 per cent permanent set, which is specified by the U. S. Navy Department\* for determination of the yield strength of cold-rolled 18-8 steel. In making the tensile test, the Berry gauge was attached to one side of the strip sample while the other was supported by a hardened ground-steel block.

\* Specification No. 47S21.

The sample was loaded, and the strain was measured with each increment of load, to determine the yield strength. After the yield strength was reached, the gauge was removed and the sample was fractured. The slope of the modulus line was determined by the experimental points. A line was then drawn parallel to the modulus line, to denote a permanent set of 0.20 per cent. The stress at the point at which this parallel line

TABLE 3.\*—*Stress-strain Data Corresponding to Fig. 4*

For steel containing 18.95 per cent Cr, 7.69 per cent Ni and 0.07 per cent C. Sample tested, 0.375-in. diameter

Stress, Lb. per Sq. In.	Curve 1. Gauge Length 2 Cm. As Cold-rolled		Curve 2. Gauge Length 2 Cm. Heated 16 Hours at 200°C. (392°F.) and Air-cooled after Stressing as Shown by Curve 1	
	Strain, In. per In.	Determined $E \times 10^{-6}$ Lb. per Sq. In.	Strain, In. per In.	Determined $E \times 10^{-6}$ Lb. per Sq. In.
0				
3,620	0.000145	25.0	0.000134	27.0
7,250	0.000280	25.9	0.000264	27.5
10,900	0.000420	25.9	0.000394	27.7
14,500	0.000564	25.7	0.000525	27.6
18,100	0.000713	25.4	0.000660	27.4
21,800	0.000860	25.4	0.000785	27.7
25,400	0.001020	24.9	0.000915	27.8
29,000	0.001180	24.6	0.001050	27.6
32,600	0.001320		0.001180	27.6
36,200	0.001510		0.001320	27.4
39,800			0.001430	27.8
43,500			0.001570	27.7
47,100			0.001700	27.7
49,000			0.001775	27.5
50,700			0.001845	27.4
52,500			0.001920	27.3
54,300			0.002000	27.1
56,100			0.002080	27.0

\* This table is printed here to illustrate the material that appears in Tables 1, 2, 6, 7 and 10. For further explanation see Note at end of paper.

intersected the stress-strain curve was taken as the yield strength. For the sake of discussion, some of the data and a few stress-strain curves obtained in the tests on the thin sections of cold-rolled 18-8 steels are given in Tables 4 and 5 and in Figs. 5 and 6. The stress-strain data for Figs. 5 and 6 are shown in Tables 6 and 7.\*

The curves of Figs. 5 and 6, obtained on thin strip using the Berry gauge, show that in the cold-rolled condition the medium-carbon 18-8 steels begin to elongate permanently when low stresses are applied, and

\* See note on page 448.

continue to do so until the metal fractures. The slope of the modulus line has been drawn as accurately as possible in accordance with the experimental points. The curves obtained by testing the same steels heated at 200°C. (392°F.) for periods of between 16 and 168 hr. exhibit

TABLE 4.—*Elastic Properties of Cold-rolled Low-carbon 18-8 Steels before and after Heating at 200°C., as Determined by Berry Gauge*

Heat No.	Constituent, Per Cent			Thick-ness of Sam-ple, In.	Re-duc-tion by Cold-rolling, Per Cent	Condition of Sample	Ob-served Pro-portion-al Limit, Lb. per Sq. In.	Yield Strength, 0.20 Per Cent Set, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elong-ation in 2 In., Per Cent	$E \times 10^{-6}$ , Lb. per Sq. In.
	Cr	Ni	C								
D73	17.00	7.54	0.05	0.03	30	As cold-rolled.	23,800	130,000	177,500	11	27.2
D73	17.00	7.54	0.05	0.03	30	Heated 24 hr. at 200°C. (392°F.) and air-cooled.	56,000	165,000	175,000	13	27.5
D73	17.00	7.54	0.05	0.03	30	Heated 64 hr. at 200°C. (392°F.) and air-cooled.	66,500	174,000	180,000	8	27.5
D73	17.00	7.54	0.05	0.03	30	Heated 72 hr. at 200°C. (392°F.) and air-cooled.	50,000	176,000	183,400	8	28.0
D73	17.00	7.54	0.05	0.03	40	As cold-rolled.	36,800	180,000	196,000	3	27.6
D73	17.00	7.54	0.05	0.03	40	Heated 24 hr. at 200°C. (392°F.) and air-cooled.	69,000	200,000	212,000	2	27.4
D73	17.00	7.54	0.05	0.03	40	Heated 64 hr. at 200°C. (392°F.) and air-cooled.	77,000	200,000	212,000	2	27.6
D73	17.00	7.54	0.05	0.03	40	Heated 72 hr. at 200°C. (392°F.) and air-cooled.	64,000	208,000	211,500	2	27.3
3	18.37	9.54	0.07	0.03	50	As cold-rolled.	49,700	156,000	173,300	6	25.7
3	18.37	9.54	0.07	0.03	50	Heated 24 hr. at 200°C. (392°F.) and air-cooled.	49,700	167,000	181,400	5	28.2
3	18.37	9.54	0.07	0.03	50	Heated 72 hr. at 200°C. (392°F.) and air-cooled.	68,500	170,000	182,000	5	27.4
3	18.37	9.54	0.07	0.03	50	As cold-rolled. <sup>a</sup>	49,400	142,500	177,800	9	29.4
3	18.37	9.54	0.07	0.03	50	Heated 72 hr. at 200°C. (392°F.) and air-cooled. <sup>a</sup>	78,800	160,000	186,200	7	28.8

<sup>a</sup> Tested in the transverse direction to rolling. Other samples tested in the longitudinal direction to rolling.

a higher proportional limit, and no difficulty is met with in determining the slope of the modulus line from the experimental points. Based on the slope of the modulus line, the modulus of elasticity of the cold-rolled steels after the heat-treatment is approximately 28,000,000 lb. per sq. in. The curves of Fig. 6 show that the improvement secured on heating at 200°C. (392°F.) occurs in both directions of rolling and makes the elastic properties of the steels more uniform in both directions. A comparison



TABLE 5.—*Elastic Properties of Cold-rolled Medium-carbon 18-8 Steels before and after Heating at 200°C., as Determined by Berry Gauge*

Heat No.	Constituent, Per Cent			Thick-ness of Sam-ple, In.	Re-duc-tion by Cold-rolling, Per Cent	Condition of Sample	Ob-served Pro-portion-al Limit, Lb. per Sq. In.	Yield Strength, 0.20 Per Cent Set, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elong-ation in 2 In., Per Cent	$E \times 10^{-4}$ , Lb. per Sq. In.
	Cr	Ni	C								
D246	17.43	7.75	0.11	0.03	30	As cold-rolled.	32,000	132,000	198,900	18.0	27.4
D246	17.43	7.75	0.11	0.03	30	Heated 8 hr. at 200°C. (392°F.) and air-cooled.	56,000	166,000	192,600	16.0	27.2
D246	17.43	7.75	0.11	0.03	30	Heated 16 hr. at 200°C. (392°F.) and air-cooled.	62,300	152,000	182,800	20.0	27.0
D246	17.43	7.75	0.11	0.03	30	Heated 24 hr. at 200°C. (392°F.) and air-cooled.	59,000	166,000	190,000	18.0	28.0
D246	17.43	7.75	0.11	0.03	30	Heated 64 hr. at 200°C. (392°F.) and air-cooled.	60,000	152,000	181,000	18.5	28.0
D246	17.43	7.75	0.11	0.03	30	Heated 168 hr. at 200°C. (392°F.) and air-cooled.	49,000	159,000	181,000	17.0	27.4
D246	17.43	7.75	0.11	0.03	40	As cold-rolled.	34,000	175,000	205,000	13.0	27.6
D246	17.43	7.75	0.11	0.03	40	Heated 8 hr. at 200°C. (392°F.) and air-cooled.	49,000	194,000	211,000	10.0	27.8
D246	17.43	7.75	0.11	0.03	40	Heated 24 hr. at 200°C. (392°F.) and air-cooled.	56,000	197,000	213,000	8.0	27.7
D246	17.43	7.75	0.11	0.03	40	Heated 64 hr. at 200°C. (392°F.) and air-cooled.	70,000	193,000	205,000	10.0	27.5
D246	17.43	7.75	0.11	0.03	40	Heated 72 hr. at 200°C. (392°F.) and air-cooled.	69,000	200,000	214,500	8.0	27.8
D246	17.43	7.75	0.11	0.03	40	Heated 168 hr. at 200°C. (392°F.) and air-cooled.	53,000	182,000	201,000	15.0	27.5
12	16.69	7.41	0.12	0.025	35	As cold-rolled.	45,000	160,000	183,700	11.0	26.0
12	16.69	7.41	0.12	0.025	35	Heated 100 hr. at 200°C. (392°F.) and air-cooled.	75,000	175,000	191,000	12.0	27.5
12	16.69	7.41	0.12	0.025	35	As cold-rolled.*	48,000	147,000	188,700	13.0	30.0
12	16.69	7.41	0.12	0.025	35	Heated 100 hr. at 200°C. and air-cooled.*	73,000	165,000	189,000	11.0	29.4
6	17.16	7.49	0.09	0.03	40	As cold-rolled.	33,500	155,500	189,000	21.0	27.2
6	17.16	7.49	0.09	0.03	40	Heated 1 hr. at 200°C. (392°F.) and air-cooled.	51,000	166,000	175,900	18.5	26.0
6	17.16	7.49	0.09	0.03	40	Heated 72 hr. at 200°C. (392°F.) and air-cooled.	58,000	182,000	192,000	10.0	28.4
6	17.16	7.49	0.09	0.03	40	Heated 168 hr. at 200°C. (392°F.) and air-cooled.	66,600	177,000	181,800	20.0	28.6
6	17.16	7.49	0.09	0.03	40	As cold-rolled.*	41,800	134,000	188,800	11.5	29.4
6	17.16	7.49	0.09	0.03	40	Heated 72 hr. at 200°C. (392°F.) and air-cooled.*	71,000	166,000	193,000	13.0	30.0

\* Tested in transverse direction to rolling. Other samples tested in the longitudinal direction to rolling.

of the curves of both figures with those of Fig. 1 shows that when stressed the heat-treated 18-8 steel samples act more like the 13 per cent Cr steel containing 0.16 per cent C than like the as-cold-rolled 18-8 steel described by Ffield.<sup>3</sup>

The data of Tables 4 and 5, which summarize the tensile properties of the steels, reveal that the improvement in elasticity is brought about without materially affecting either the tensile strength or ductility. In

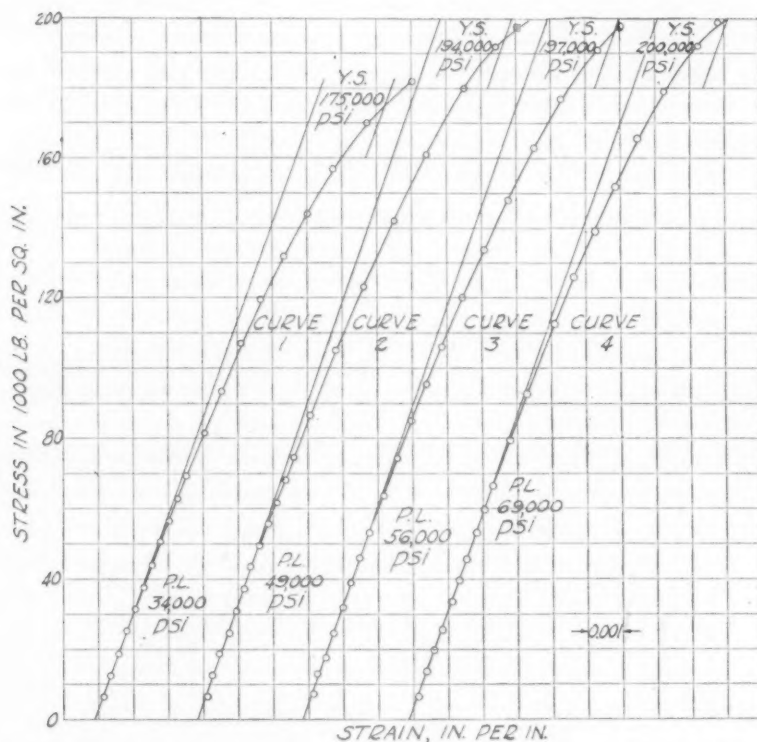


FIG. 5.—STRESS-STRAIN CURVES FOR 0.03-INCH THICK STRIP REDUCED 40 PER CENT BY COLD-ROLLING OF STEEL CONTAINING 17.43 PER CENT CHROMIUM, 7.75 PER CENT NICKEL AND 0.11 PER CENT CARBON.

Samples tested in direction of rolling.

Curve 1. As cold-rolled.

Curve 2. Heated 8 hours at 200°C. (392°F.) and air-cooled.

Curve 3. Heated 24 hours at 200°C. (392°F.) and air-cooled.

Curve 4. Heated 72 hours at 200°C. (392°F.) and air-cooled.

addition, the surfaces of the thin cold-rolled strip were not covered with a heavy oxide coating but were tinted slightly yellowish, and unless they were compared side by side with an unheated sample it was difficult to tell whether the color of the cold-rolled surface had changed. The slightly yellowish colored oxide was readily removed by dipping in a hot 20 to 30 per cent nitric acid solution.

Thus far nothing has been said about the effect of the 200°C. (392°F.) treatment on properties other than those described by the tensile tests. In operation, light-weight, high-strength structures are subject to alter-

nating stresses, which produce fatigue; so the effect of the treatment on the previously described cold-worked 18-8 steel bar was investigated in a Krouse testing machine rotating at 6500 r.p.m. Standard-sized samples,  $1\frac{7}{8}$  in. long with  $\frac{1}{4}$ -in. end sections, having a reduced section 0.125 in. in diameter, were tested. The data are given in Table 8.

In the as-cold-worked condition the 18-8 steel, which, as previously shown, has a tensile strength of 140,300 lb. per sq. in., resisted successfully

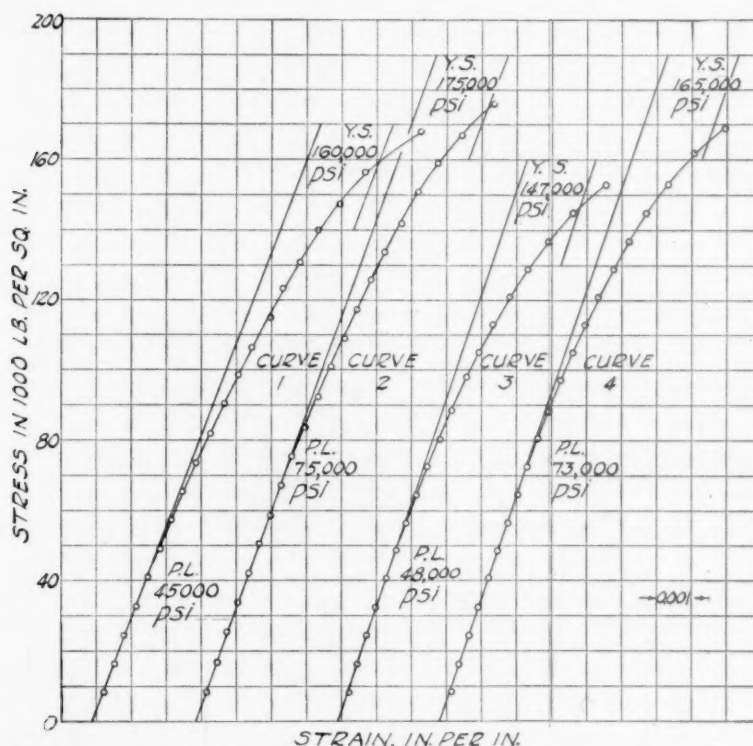


FIG. 6.—STRESS-STRAIN CURVES FOR 0.025-INCH STRIP REDUCED 35 PER CENT BY COLD-ROLLING OF STEEL CONTAINING 16.69 PER CENT CHROMIUM, 7.41 PER CENT NICKEL AND 0.12 PER CENT CARBON.

Curve 1. As cold-rolled. Tested in the direction of rolling.

Curve 2. Heated 100 hours at 200°C. (392°F.) and air-cooled. Tested in direction of rolling.

Curve 3. As cold-rolled. Tested across direction of rolling.

Curve 4. Heated 100 hours at 200°C. (392°F.) and air-cooled. Tested across direction of rolling.

a fatigue stress of 85,000 lb. per sq. in., whereas after treatment at 200°C. (392°F.) the same steel withstood a stress of 92,000 lb. per sq. in. The test was discontinued at this point because it represented the capacity of the machine for the standard-sized sample. It seemed inadvisable to test a smaller sample machined from the cold-rolled  $\frac{1}{2}$ -in. thick by  $\frac{3}{4}$ -in. wide bar. The results, however, are sufficient to show that the fatigue resistance of the metal was not impaired, but was substantially improved by the heat-treatment.

In another set of experiments, sections of the same steel were machined to Izod impact samples. Some of these were given the low-temperature

treatment and others were left as cold-worked. The samples were tested for toughness, and it was found that the toughness of the steel had been increased somewhat by the treatment (Table 9). This definitely

TABLE 8.—*Fatigue Endurance Tests on Cold-worked 18-8 Steels*

Constituent, Per Cent			Condition of Metal	Stress, Lb. per Sq. In.	Cycles <sup>b</sup>	Remarks
Cr	Ni	C				
18.95	7.69	0.07	As cold-worked. <sup>a</sup>	83,000	10 × 10 <sup>6</sup>	No failure.
18.95	7.69	0.07	As cold-worked. <sup>a</sup>	85,000	11.4 × 10 <sup>6</sup>	No failure.
18.95	7.69	0.07	As cold-worked. <sup>a</sup>	86,000	0.199 × 10 <sup>6</sup>	Failure.
18.95	7.69	0.07	Heated 72 hr. at 200°C. (392°F.) and air-cooled.	85,000	10 × 10 <sup>6</sup>	No failure.
18.95	7.69	0.07	Heated 72 hr. at 200°C. (392°F.) and air-cooled.	88,000	10.494 × 10 <sup>6</sup>	No failure.
18.95	7.69	0.07	Heated 72 hr. at 200°C. (392°F.) and air-cooled.	92,000	10 × 10 <sup>6</sup>	No failure.

<sup>a</sup> Percentage of cold reduction unknown.

<sup>b</sup> As in testing steels in general, 10 × 10<sup>6</sup> cycles was accepted as satisfactory.

indicated that heating at 200°C. (392°F.) does not cause carbide precipitation, because in general such phenomena are accompanied by a decrease in toughness. Also, the Brinell numbers of the metal before and after treatment were approximately the same.

TABLE 9.—*Impact Toughness of Cold-rolled 18-8 Steel*

Constituent, Per Cent			Condition of Metal	Izod Impact Value, Ft.-lb.	Brinell Hardness Number
Cr	Ni	C			
18.95	7.69	0.07	As cold-worked.	33, 35	302
18.95	7.69	0.07	Heated 72 hr. at 200°C. (392°F.) and air-cooled.	38, 40	311

Corrosion experiments have been made on thin sections of the cold-rolled 18-8 steels given various degrees of cold-work both before and after heating at 200°C. (392°F.). These have included exposure to spray from a 20 per cent sodium chloride solution, boiling 65 per cent nitric acid, and a boiling solution consisting of approximately 16 per cent by weight of sulphuric acid and 6 per cent by weight of copper sulphate. After 200-hr. exposure to the spray from the 20 per cent sodium chloride solution, some of the samples were stained and pitted and others were free of both defects, but no difference was observed in the heated and unheated samples. In the tests with boiling nitric acid, which extended over five 48-hr. boiling periods, the weight losses before and after the treatment



were entirely comparable, showing that the heat-treatment did not decrease the resistance of the cold-worked metal to this acid. Particular attention has been paid to the question of whether the treatment renders the steels subject to intergranular corrosion. After several hundred hours exposure to the boiling acidified copper sulphate solution, no instance has been noted in which a sample heated at 200°C. (392°F.) has exhibited any signs of susceptibility to intergranular attack. This result is pertinent. It shows that the treatment can be applied to cold-rolled 18-8 steels without stabilizing elements, which from the standpoint of economics is important.

TABLE 10.—*Tests Corresponding to Fig. 7*

Tie rod made of steel containing 18.53 per cent chromium, 13.57 per cent nickel, 3.04 per cent molybdenum and 0.06 per cent carbon

PART A.<sup>a</sup>—PHYSICAL PROPERTIES OF STEEL IN COLD-WORKED, AND COLD-WORKED AND HEAT-TREATED CONDITIONS

	Curve 1. Gauge Length 2 In. As Cold-worked	Curve 2. Gauge Length 2 In. Heated 72 Hr. at 200°C. (392°F.) and Air-cooled
$E \times 10^{-6}$ .....	25.4	27.2
Proportional limit, per lb. per sq. in. ....	42,000	80,000
Yield strength, lb. per sq. in. (0.20 per cent set).....	147,000	172,000
Tensile strength, lb. per sq. in. ....	183,000	190,000
Elongation, per cent in 2 in. ....	9	7

<sup>a</sup> See note at end of paper.

Samples of cold-rolled 18-8 steels containing columbium and molybdenum have been investigated. The improvement in the elastic properties of the columbium-bearing 18-8 steels and the molybdenum-bearing 18-8 steels obtained by heating at 200°C. (392°F.) is as great as that obtained with the plain 18-8 steels. This is shown by the data of Table 10 and Fig. 7, obtained on samples of a molybdenum-bearing 18-8 steel tie rod ( $\frac{3}{8}$ -24 size) using the Berry gauge and the procedure employed in testing the thin cold-rolled 18-8 steel strip samples. This tie rod was fabricated commercially, and information on the percentage of cold reduction of the metal is not available. It is important to emphasize that the cold-rolled 18-8 steels containing molybdenum are more resistant to pitting than the plain 18-8 steels, and with the improvement in elastic properties the former steels are far more suitable for use in light-weight construction when resistance to sea water is needed.

#### SUMMARY

This investigation has shown that the modulus of elasticity of wrought annealed 18 per cent Cr, 8 per cent Ni steels is approximately 28,000,000

lb. per sq. in. and the proportional limit is on the order of 20,000 lb. per sq. in. with a tensile strength between 80,000 and 90,000 lb. per sq. inch.

In confirmation of work of other investigators, it has been found that even though the tensile strength of the annealed 18-8 steel can be greatly increased by application of cold-work, the indicated proportional limit of the metal remains low, and the modulus of elasticity is somewhat lower than that of the annealed steel, especially in the direction of rolling. In the transverse direction to rolling the cold-rolled steels have a some-

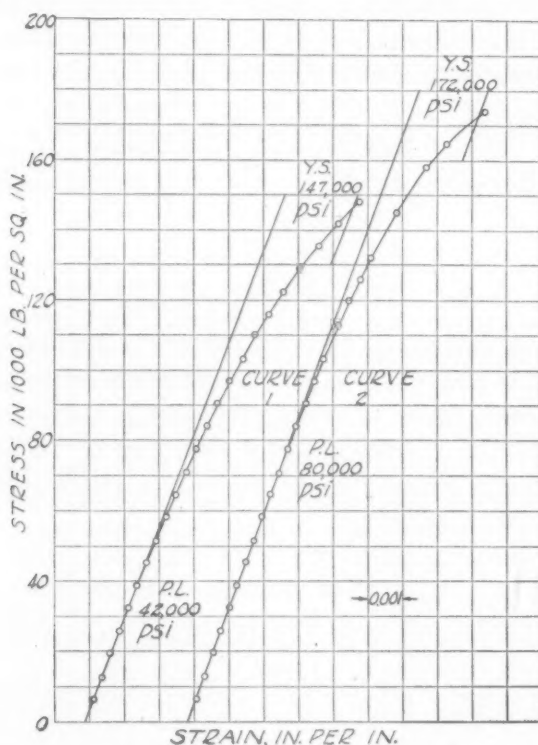


FIG. 7.—STRESS-STRAIN CURVES FOR TIE ROD OF STEEL CONTAINING 18.53 PER CENT CHROMIUM, 13.57 PER CENT NICKEL, 3.04 PER CENT MOLYBDENUM AND 0.06 PER CENT CARBON.

Curve 1. As cold-worked.

Curve 2. Heated 72 hours at 200°C. (392°F.) and air-cooled.

what higher proportional limit with a modulus of elasticity equal to that in the annealed condition.

It has been further shown that if the cold-worked metal is heated to about 200°C. (392°F.) and air-cooled it will act more normally when stressed, and exhibit a considerably higher observed proportional limit and yield strength (0.20 per cent set) with a modulus of elasticity of approximately 28,000,000 lb. per sq. in. at room temperature. This treatment produces increased fatigue resistance and improves toughness somewhat without rendering the steels subject to intergranular corrosion or reducing their resistance to general corrosion. The treatment does not

impair tensile strength, ductility or the bright cold-rolled surface. Only a slight yellowish coating develops during the heating period, and that is readily removed, if necessary, by a dip into hot nitric acid solution.

The elastic properties of cold-rolled 18 per cent Cr, 8 per cent Ni steels containing either columbium or molybdenum are likewise improved by heat-treating under the same conditions.

It must be emphasized that the time factor is most important in bringing about the improvement, and that unless the heating period is long enough the improvement in elastic properties will be neither substantial nor uniform. From the standpoint of practice it is suggested that the heating period consume at least 8 hr. but no more than 100 hr., in the range from 200° to 250°C. If these conditions are adhered to in treating plain or modified cold-rolled 18-8 steels, the opinion may be expressed that they are without a peer for use in light-weight, high-strength structures.

#### NOTE

An appendix to this paper, showing complete Tables 1, 2, 6, 7 and 10, may be obtained from American Documentation Institute, 2101 Constitution Avenue, Washington, D. C., by ordering Document 1323, remitting 27¢ for copy in microfilm (read enlarged to full size on reading machines now widely available), or 90¢ for copy in paper photoprints legible without mechanical aid.

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## DISCUSSION

(G. B. Waterhouse presiding)

P. R. KOSTING,\* Watertown, Mass.—This work again shows that plain cold-worked 18-8 cannot be simply heated at any temperature in the range 300° up to over 600°C. to relieve internal stresses without detrimental effect on its corrosion resistance. The work of Rollason indicates that for one particular analysis the range extends from 425° to 850°C. when time at temperature is long. The American Society for Testing Materials Specification (A198-39) for castings suggests 2 hr. at 425°C. for relief of quenching strains. Limited experience at Watertown Arsenal showed that up to 6 hr. at 400°C. was not enough for sufficient relief of strains in some cases. Though 8 hr. at 200°C. is sufficient to raise markedly the proportional limit, sufficient relief of internal strains may not be obtained.

When stress-relief-annealed prior to test, experiment at Watertown Arsenal showed that the effect of progressive cold-work on 18-8 was to raise the proportional limit at a rate, with respect to degree of cold-work, that was faster than the effect on tensile strength.

W. B. SEENS,† Kearny, N. J.—In any paper on the elastic properties of 18-8 there should be some consideration of the work of M. F. Sayre<sup>12</sup> and of McAdam and Mebs.<sup>13</sup> The former has shown that Hooke's law is only an approximation and that the stress-strain line is probably curved throughout its entire length. On this basis there can be no true proportional limit, therefore any so-called proportional limit is not a fundamental property of the material though it may be significant as a relative value provided that it is observed under strictly comparable conditions. In other words, any value of stress assigned as a proportional limit depends upon the sensitivity of the measurement of the strain, being lower, the more sensitive the measuring device is. The present paper adduces evidence to this effect, when we compare the values of proportional limit obtained with the Huggenberger extensometer with those observed by the considerably less sensitive Berry gauge, the latter values being considerably higher than the former. It is true that different steels and different specimens are involved, but these differences do not invalidate the general comparison. Again both the proportional limit and the ratio of proportional limit to tensile strength are lessened by cold-rolling, according to the data of Table 1 based on Huggenberger measurement, but increased by cold reduction, according to the data of Table 4 based on the Berry gauge.

McAdam and Mebs, who made exhaustive studies of the modulus of elasticity of 18-8, pointed out that the stress-strain relationship alone gives only an incomplete picture of the elastic properties. Since the stress-strain line is curved even at very low stresses, they emphasize the limiting modulus at zero stress and the use of a constant to indicate the change of modulus with stress. This modulus at zero stress is obtained by extrapolating the stress-strain curve observed on an axially loaded specimen, and is the only value having a fundamentally sound basis. Their values of modulus on initial loading range from 32.4 million lb. per sq. in. for annealed 18-8 to 27.4 million lb. per sq. in. for 18-8 cold-rolled to a tensile strength of 260,000 to 280,000 lb. per sq. inch.

\* Watertown Arsenal.

† Research Laboratory, U. S. Steel Corporation.

<sup>12</sup> M. F. Sayre: *Trans. Amer. Soc. Mech. Engrs.* (1934) 56 (7).

<sup>13</sup> D. J. McAdam and R. W. Mebs: *Tensile Elastic Properties of 18-8 Chromium-nickel Steel as Affected by Plastic Deformation. Rept. No. 670, National Advisory Committee for Aeronautics, 1939.*



McAdam and Mebs also demonstrated that slight prestressing of cold-worked 18-8 may bring about a considerable increase of its elastic strength, so that the high proportional limit of curve 2 of Fig. 4 is probably attributable to both prestressing and heat-treatment, and not to heat-treatment alone, as the authors imply. It would be interesting to have data on similar specimens prestressed to the same degree but not heat-treated; for it would then be possible to separate the effects of prestressing and of heat-treatment. Such data would appear particularly important in connection with low-temperature stress-relief annealing of fabricated sections, which are cold-worked during fabrication.

Do the results reported in this paper refer to single specimens or are they average values from a number of tests? Some indication of the consistency of results would be of interest, especially in view of the uncertainty attaching to any estimate of the apparent proportional limit.

We wish to compliment the authors on their development of a practical means of increasing the apparent proportional limit of 18-8, and feel that a continuation of this work will go far to remove the stigma attached to 18-8 on account of its apparent excessive yielding at low stresses.

W. A. MUDGE,\* New York, N. Y.—Results similar to those reported by Franks and Binder for stainless steels have been observed in hot-worked and in cold-worked Monel.<sup>14</sup> Studies by Dr. Kosting with high-strength, hot-rolled Monel plates, some of which had been cold-worked 10 per cent after hot-rolling, showed definite increases in yield strength, 0.00 per cent offset (proportional limit), of 25 to 70 per cent, resulting from heating in a temperature range of 800° to 1110°F., that the maximum increase was effected by a temperature of 1020° to 1110°F., and that the greater the extent of previous cold-work, the lower was the temperature at which the maximum proportional limit values were obtained. It was also apparent that the maximum proportional limit was accompanied by slight decreases in yield strength, 0.20 per cent offset, and in ultimate tensile strength, and by a slight increase in elongation.

In the discussion of Dr. Kosting's paper, the writer (ref. 14) offered similar experimental data for 1½-in. dia. cold-drawn Monel rods. They showed that an increase of 50 per cent in proportional limit resulted from thermal treatment at the optimum temperature of 570°F., and was accompanied by a slight decrease in yield point and no appreciable changes in the ultimate tensile strength, elongation or reduction of area. The lower optimum temperature, in the case of this more severely cold-worked material, verified Dr. Kosting's results. Increases in proportional limit of 100 per cent—i.e., 40,000 to 80,000 lb. per sq. in.—have been obtained with 1-in. dia. cold-drawn Monel rods by similar thermal treatment. Similar results have been observed in our laboratories with nickel at 575°F. and with Inconel at 800°F.

The phrase "stress-relief annealing" as heretofore used may not accurately describe the observed results. "Stress-relief annealing" requires softening, either partial or total. "Stress-equalizing annealing" is considered a preferable term to describe a thermal treatment, below the temperature for soft or temper annealing, which equalizes, or homogenizes, stresses so as to produce the optimum combination of proportional limit with ductility (elongation and reduction of area) in the material, even though the result may be accompanied by slight decreases in yield and tensile strengths.

The writer believes it desirable to consider whether or not the improved elastic strength resulting from low-temperature thermal treatment is due to age-hardening or to stress equalization.

\* Development and Research Division, The International Nickel Co., Inc.

<sup>14</sup> P. R. Kosting: Stress-relief Annealing High-strength Monel Plate. *Proc. Amer. Soc. Test. Mat.* (1936) **36**, pt. II, 222.

The fact that similar results have been observed with alloys as dissimilar as austenitic 18% stainless steel and Monel and Inconel, and with a commercially pure metal like nickel, leads to the conclusion that the phenomenon is more likely associated with the equalizing, or homogenizing, effects of temperature upon internal stress than with a precipitation-hardening effect.

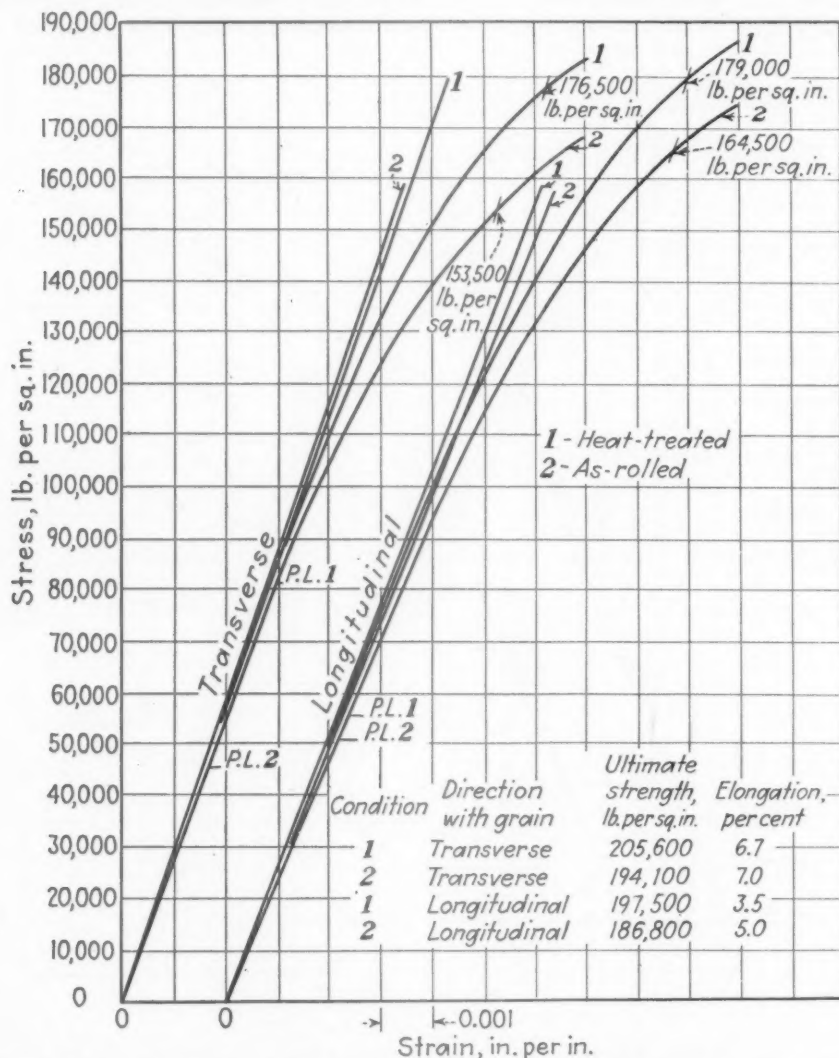


FIG. 8.—COMPARISON OF TENSILE PROPERTIES OF AS-ROLLED AND HEAT-TREATED 18-8 STEEL SHEET. 0.020 INCH THICK. WRIGHT FIELD.

E. M. MAHLA,\* Bethlehem, Pa.—Have the authors considered the effect of strain-aging as an explanation of their results? Since the portion of the stress-strain curve outside the elastic range is dependent upon the rate of work-hardening for its shape, it is conceivable that in a metal with as strong work-hardening characteristics as 18-8 the stress-strain curve might be little affected outside the elastic range by strain-aging while at the same time the strain-aging might materially increase the resistance to initial deformation.

\* Graduate Student, Lehigh University.

It is known that when mild steel is strained beyond its yield point and immediately retested it is found that the limit of proportionality is greatly reduced. However, upon standing at room temperature the elastic properties are recovered and may even become better than those of the original specimen. Such a result is supposed to be due to the so-called strain-aging, which must be of the nature of a fine precipitate similar in kind to that produced by age-hardening. Recovery of this type may be

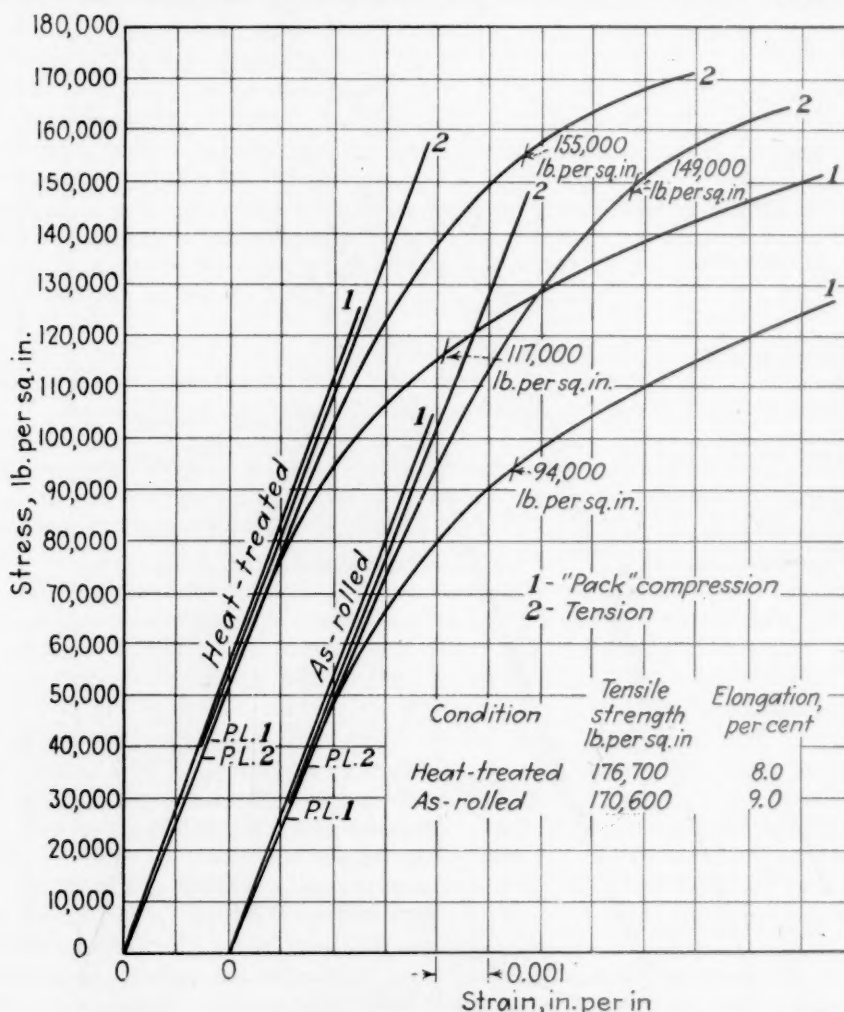


FIG. 9.—COMPARISON OF TENSILE AND COMPRESSIVE PROPERTIES OF 18-8 STEEL SHEET, HEAT-TREATED AND AS-ROLLED. LONGITUDINAL WITH GRAIN, 0.034 INCH THICK. WRIGHT FIELD.

hastened by heating. If the phenomenon of strain-aging involves precipitation it must necessarily involve diffusion. It seems possible that the rates of diffusion of the constituents of the precipitating phase in 18-8 are so slow at room temperature that once the elastic properties are destroyed by cold-work they may never be recovered unless strain-aging precipitation is accelerated by heating to the temperatures recommended by the authors. Such a precipitation might conceivably take place below the range of visible carbide precipitation and result in the improvement of the elastic properties outlined in the present paper.

F. B. FULLER,\* Dayton, Ohio.—Tests have been made recently at Wright Field on light-gauge cold-rolled 18-8 type corrosion-resistant steel in the as-rolled condition and after aging at 440°F. (225°C.) for 24 hr. The material had an approximate chemical analysis of 0.11 C, 18 to 19 Cr and 8.5 Ni.

Although results indicate trends in mechanical and corrosion-resistant properties comparable to those reported in the paper, the increases in the tangent proportional limit, Table 11, were not as marked. The tension tests were made on standard flat

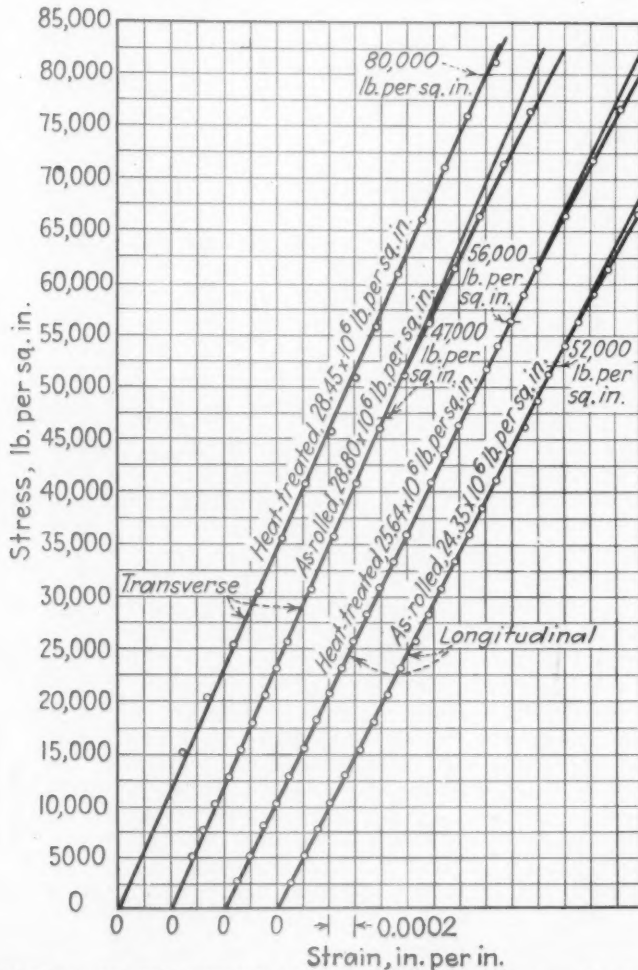


FIG. 10.—MODULUS OF ELASTICITY AND PROPORTIONAL LIMIT IN TENSION FOR 18-8 STEEL SHEET 0.020 INCH THICK. WRIGHT FIELD.

specimens with Templin self-aligning grips and paired one-inch Tuckerman optical strain gauges, which are more sensitive than the Berry gauges. The tangent proportional limits, determined from stress-strain curves drawn to a relatively large scale and reduced to approximately  $\frac{1}{4}$  in. equal to 1 in. in Figs. 10 and 11, were comparable to those determined by the strain-difference method, ref. 15 and Fig. 12. The propor-

\* Materials Testing Engineer, Wright Field.

<sup>15</sup> L. B. Tuckerman: Discussion on Proportional Limit. *Proc. Amer. Soc. Test. Mat.* (1939).



TABLE 11.—*Tensile and Compressive Properties of 18-8 Corrosion-resistant Steel Sheet*

Direction to Rolling	Thick- ness, In.	Condition	Proportional Limit, Lb. per Sq. In.		Yield Strength, Lb. per Sq. In., 0.2 Per Cent Set	Ultimate Strength, Lb. per Sq. In.	Modulus of Elasticity × 10 <sup>6</sup> , Lb. per Sq. In.	Elongation in 2 In., Per Cent	Hardness	
			Tangent	0.01 Per Cent Set					Standard Rockwell A	Superficial 30N
TENSILE VALUES										
Transverse .....	0.020	As-rolled	47,000	75,000	153,500	194,100	28.8	7.0	69.0	60.5
Transverse .....	0.020	Heat-treated	80,000	107,500	176,500	205,600	28.4	6.7	70.0	62.0
Longitudinal .....	0.020	As-rolled	52,000	76,000	164,500	186,800	24.4	5.0		
Longitudinal .....	0.020	Heat-treated	56,000	95,000	179,000	197,500	25.6	3.5		
Longitudinal .....	0.034	As-rolled	36,000	65,000	149,000	170,600	25.7	9.0	70.0	62.0
Longitudinal .....	0.034	Heat-treated	38,000	79,000	155,000	176,700	27.0	8.0		
COMPRESSIVE VALUES										
Longitudinal .....	0.034	As-rolled	26,000	41,000	94,000		27.0			
Longitudinal .....	0.034	Heat-treated	41,000	66,000	117,000	156,200	27.8			
RATIO OF COMPRESSIVE TO TENSILE VALUES										
Longitudinal .....	0.034	As-rolled	0.72	0.63	0.63					
Longitudinal .....	0.034	Heat-treated	1.08	0.84	0.75	0.88				

tional limits (0.01 per cent offset) were obtained from Figs. 10 and 11, extended to the required size.

The heat-treatment produced an appreciable difference in the stress-strain curves up to the yield point (0.20 per cent offset), the proportional limit (0.01 per cent offset) being considerably higher, Table 11 and Figs. 8 and 9.

The difference in modulus of elasticity for transverse and longitudinal material, 0.020 in. thick (Fig. 10) has been noted in previous tests at this laboratory. The modulus of elasticity is increased by the heat-treatment.

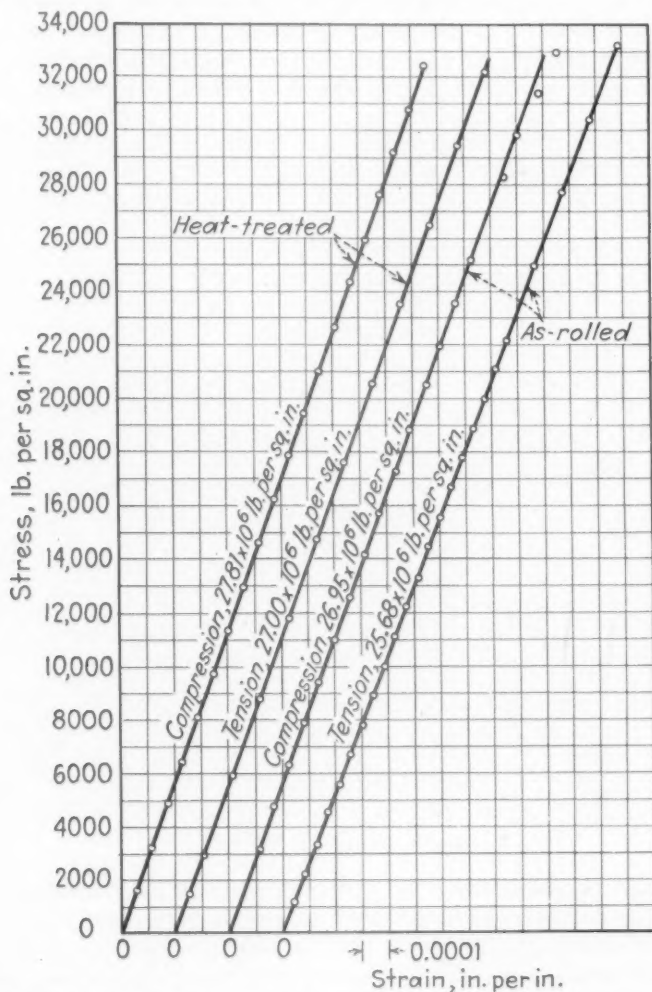


FIG. 11.—TENSILE AND COMPRESSIVE CURVES FOR MODULUS OF ELASTICITY OF 18-8 STEEL SHEET, LONGITUDINAL WITH GRAIN, 0.034 INCH THICK. WRIGHT FIELD.

The compressive data are interesting in showing their relationship to tensile properties and the effects of heat-treatment. The increase in compressive properties is marked and occurs in the range in which short-column data are affected. The tests were made in a "pack" jig (Fig. 13) similar to that developed by the Bureau of Standards.<sup>16</sup>

<sup>16</sup> C. S. Aitchison and L. B. Tuckerman: The "Pack" Method for Compressive Tests on Thin Specimens of Material Used in Thin-wall Structures. National Advisory Committee for Aeronautics, Rept. No. 649 (1939).

W. H. SWANGER,\* Washington, D. C.—The conclusions of the authors as to the influence of their low-temperature heat-treatment on the elastic properties of cold-rolled stainless steel were based on the relationship between stress and total strain. It was shown by McAdam and Mebs (ref. 13) that this relationship gives an incomplete view of the elastic properties of a metal. Consideration should be given to both the stress-strain and the stress-set relationships. From these relationships is derived the elastic stress-strain curve, from which the modulus of elasticity, and its stress coefficient should be obtained.

The present authors' estimates of "proportional limits" are merely estimates, based upon their plots of total strain. Actually, proportional limits as usually defined are not technically determinable. Stresses causing specific values of offset on the stress-strain curve (total strain), or specified values of permanent set ("proof" stress) shown by the stress-set curve, can be determined. With modern extensom-

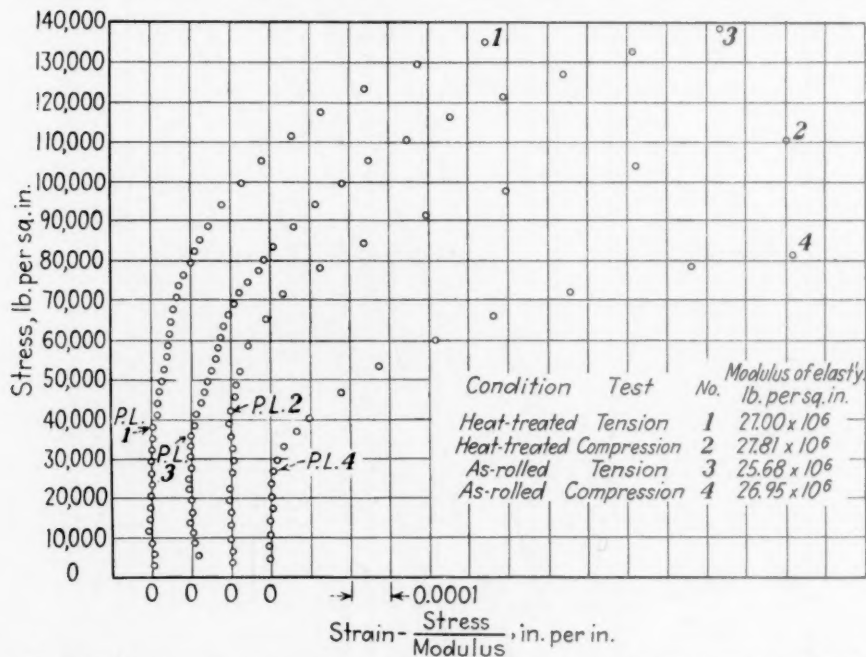


FIG. 12.—DIFFERENCE CURVES FOR 18-8 STEEL SHEET, LONGITUDINAL, 0.034 INCH THICK. WRIGHT FIELD.

eters, strain or set values as small as 0.001 per cent can be determined accurately. Such determinations fulfill the requirements implied in determinations (?) of the so-called proportional limit. However, the authors' procedure of measuring extensions with a hand strain gauge attached to one side of a strip specimen does not yield trustworthy results for such purposes.

Results of a few experiments soon to be published<sup>17</sup> indicated that the heat-treatment advocated by the present authors tends to straighten the stress-strain curve, somewhat as indicated in the present paper, but does not raise the "proof" stresses appreciably above the values obtained when the material (18-8) is annealed for only 30 min. at the same temperature.

\* Metallurgist, National Bureau of Standards.

<sup>17</sup> D. J. McAdam and R. W. Mebs: Tensile Elastic Properties of Typical Stainless Steels and Non-Ferrous Metals, as Affected by Plastic Deformation and by Heat Treatment. National Advisory Committee for Aeronautics Report No. 696. In press.

It is to be hoped that additional investigations will be made of this interesting phenomenon to determine the magnitude of the effects of the low-temperature heat-treatment upon the elastic strength properties of cold-rolled stainless steel.

R. FRANKS AND W. O. BINDER (authors' reply).—It is a pleasure to learn that tests made at the Watertown Arsenal on cold-worked 18-8 steel given a stress-relief treatment confirm those shown in the paper. We agree that 8 hr. at 200°C. may not be sufficient to relieve all internal stress present in cast metal.

Mr. Seens is correct in stating that the assigned value for the proportional limit of a steel is dependent on the sensitivity of the extensometer employed. When the data are obtained under comparable conditions, however, it affords a relative means for distinguishing differences due to heat-treatment, for instance.

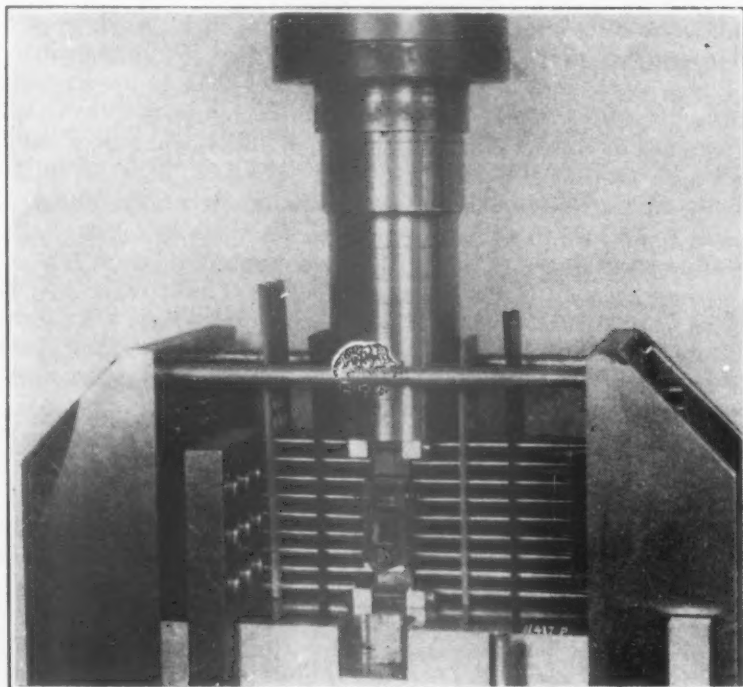


FIG. 13.—“PACK” COMPRESSION JIG WITH SPECIMEN ASSEMBLED FOR TEST.

The value of  $27.4 \times 10^6$  lb. per sq. in. for the modulus of cold-worked 18-8 steel as determined by McAdam and Mebs is in substantial agreement with the data shown in Fig. 3 (curve 2) and Fig. 4 (curve 2). The value of  $32.4 \times 10^6$  lb. per sq. in. for the modulus of elasticity of annealed 18-8 steel is higher than we have ever obtained. It has been our experience that the modulus value for annealed metal is between 28 and  $29 \times 10^6$  lb. per sq. in. In addition, it has not been our experience that the annealed 18-8 steel exhibits a stress-strain curve that is curved at all stresses. An extrapolation to zero stress therefore would not give values greatly in excess of that obtained by drawing the actual tangent line.

No tests were made on samples prestressed and not subsequently heat-treated. It is believed that in most cases of fabricated sections, the deformation of the metal greatly exceeds the amount shown by McAdam and Mebs as being effective in relieving internal stress.

The results reported in the paper refer to single specimens, although a sufficient number of duplicate tests were made to show that the improvement in elastic proper-



ties was reproducible. An indication of the consistency of results may be obtained by examining curves 2 and 3 in Fig. 1, and curve 1 in Fig. 4. The results of tests made with a Berry gauge are subject to greater variation owing to the extreme difficulty in obtaining good seating of the extensometer and to some curvature of the samples. Test results shown in Table 4 indicate the reproducibility that may be expected using a Berry gauge. The yield strength taken at 0.2 per cent set is unquestionably more easily reproducible, is less affected by the accuracy of the extensometer, and consequently is generally a more reliable value.

Mr. Mudge raises the question of terminology in describing the results reported in the paper. The term "stress-equalizing annealing" implies that there is no relief of internal stress obtained by heat-treatment below the recrystallization temperature. This interpretation is not shared by the authors. It is our belief that time as well as temperature must be considered; hence it should be possible to decrease internal stress at low temperature if the time of holding is long enough.

We are in complete agreement with Mr. Mudge that the improvement in elastic properties is due to changes in internal stress rather than to age-hardening. This belief is substantiated (as pointed out by Mr. Mudge) by the fact that similar results have been obtained on several different metals and alloys, which does not agree with Mr. Mahla's hypothesis.

It is gratifying to receive the discussion submitted by Mr. Fuller. His data obtained using a more sensitive gauge than the Berry are in substantial agreement with the results shown in the paper for the yield strength taken at 0.2 per cent set. Although the improvement in the tangent proportional limit value after heat-treatment is not so marked, it is significant that the trend is higher. On the other hand, the proportional limit taken at 0.01 per cent set and the yield strength taken at 0.2 per cent set are definitely higher, showing that the curvature of the stress-strain curve to the yield strength is decreased as a result of the heat-treatment. The data obtained by Mr. Fuller also show that the modulus of elasticity is increased by the heat-treatment. The differences in properties of the steel when measured longitudinally and transverse to the direction of rolling confirm tests made by the authors.

Mr. Fuller has included important data on the compressive properties of cold-rolled 18-8 steel strip using the pack test method. His data are in agreement with the results of compression tests made by the authors on cold-drawn 18-8 steel bars and tubes, and on cylindrical tubes formed from cold-rolled 17-7 and 18-8 steel strip. As Mr. Fuller has shown, the compressive yield strength in the as-rolled condition measured longitudinal to the direction of rolling is only 63 per cent of the tensile yield strength measured in the same direction with respect to rolling. The low-temperature heat-treatment increases the value to 75 per cent, which, as Mr. Fuller points out, is a substantial gain in short-column work. An improvement in the long-column range would also be effected, owing to the higher modulus value. The compressive properties of cold-rolled 18-8 steel have been under investigation by the authors for some time. It is believed that the amount of cold-work given the 18-8 steel is an important factor, and this point must be completely investigated before an optimum combination of physical properties in tension and compression can be obtained.

In answer to Mr. Swanger's discussion, it must be pointed out that for most purposes the tangent modulus derived from the conventional stress-strain curve has proved to be sufficiently accurate for use in the design of structures. Except for theoretical purposes, there does not seem to be any reason for using a modulus value determined from a derived elastic stress-strain curve for the 18-8 steel. The importance attached to the latter modulus is yet to be proved in the practical application of the steel. Although periods as short as 30 min. at 200°C. may result in improvement of the steel, it should be emphasized that uniform results cannot be obtained with so short a period of heating.

## Effects of Temperature of Pretreatment on Creep Characteristics of 18-8 Stainless Steel at 600° to 800°C.

By CHARLES R. AUSTIN\* AND CARL H. SAMANS,\* MEMBER A.I.M.E.

(New York Meeting, February 1940)

IN an earlier series of studies on 18-8 stainless steel at 600°, 700°, and 800°C.<sup>1</sup> one pretreatment was used throughout; viz., 15 min. in hydrogen at 950°C., followed by an air quench. Several manufacturers of this alloy since have expressed doubt as to the suitability of the temperature employed, recommending instead the more customary Strauss treatment as promising superior results. In this subsequent investigation on the effects of the temperature of pretreatment several interesting points have arisen, which are described in this paper.

Previous work on our equipment had shown a marked difference between alloys of "similar chemical composition" that had been manufactured by different companies. Accordingly, one mill-bar length was selected from which to prepare all specimens. It could then be assumed that any marked differences in creep characteristics would be due to effects resulting from variations in the pretreatment of the alloy.

The material was furnished by the Allegheny-Ludlum Steel Co. in the form of  $\frac{5}{16}$ -in. dia. rod, finished by air cooling from a mill anneal at 1950°F. (1066°C.). It was analyzed only for the elements shown: carbon, 0.07 per cent; chromium, 18.73; nickel, 9.46; manganese, 0.40.

Three pretreating temperatures were chosen, the specimens being held for 15 min. in hydrogen at either: (1) 1150°C., to conform to the recommended Strauss treatment; (2) 950°C., to compare with the results of previous tests; or (3) 750°C., to initiate precipitation of carbides in the material before testing. As the test cross sections were only  $\frac{1}{8}$ -in. dia., air cooling followed the annealing treatment. These treatments permitted two direct comparisons: (1) between the 1150° and 950°C. treatments to indicate the effect of grain size when all carbides were probably in solution at the start of the test; and (2) between the 950° and 750°C. treatments to indicate the effect of carbide "nucleation" for similar grain sizes.

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Manuscript received at the office of the Institute Dec. 1, 1939. Issued as T.P. 1181 in METALS TECHNOLOGY, June 1940.

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<sup>1</sup> References are at the end of the paper.

Dilatometric observations and metallographic studies supplemented the deformation tests.

#### DEFORMATION STUDIES

Tensile deformation tests were carried out at 600°, 700°, and 800°C. using specimens 20 in. long with a 4-in. gauge section  $\frac{1}{8}$  in. in diameter. Spring loading was used and loads were applied successively in 2000-lb. per sq. in. increments under the assumption that once the elongation-time curve had attained a steady rate for any one load its slope was a good approximation to the true secondary creep rate for those conditions. Previous work had indicated that this assumption was essentially correct. No loads of greater than 10,000 lb. per sq. in. were used, and for the higher temperatures tests were confined to even lighter loads. Tests at any one load were continued for periods of between 10 and 24 days, depending upon the character of the elongation-time curve. Consequently, for the higher loads the specimens actually were held at temperature for times approximating 2100 hr. at the lowest temperature and 1000 hr. at the highest temperature.

#### TESTS AT 600°C.

In the tests at 600°C., the results of which are shown graphically in Fig. 1, the similarity of the curves representing the three different pretreatments can readily be seen. Within the time limits of the test the smallest creep rate determinable with the apparatus used was about 0.01 per cent per 1000 hr. This value was obtained by taking three or four readings a day with a micrometer whose accuracy was 0.0001 in., and drawing a statistical curve through these points. When values as low as 0.01 per cent per 1000 hr. are recorded, the majority of the readings were unchanged and the remainder showed maximum variations of 0.0002 in., so that the best line had a slope about as shown. Where no essential variation could be detected, a value of "less than 0.01 ( $<0.01$ ) per cent per 1000 hr." was reported.

Table 1 lists the creep rates measured in all of these tests, and gives also, for comparison, the rates found previously for another lot of material made by the same manufacturer (series AMK) as well as the spread of results reported in the earlier paper<sup>1</sup> for 18-8 stainless steels of "similar chemical composition" but made by different companies. The latter data are recorded as maximum and minimum for pretreatment at 950°C. (last two columns in Table 1). It is interesting that the agreement between tests on material supplied three or four years ago, AMK series, and the present data is quite satisfactory.

The occurrence of "negative creep" or decrease in length of the specimen in the two days immediately following the application of the first load of 2000 lb. per sq. in. is an interesting feature of these deformation studies. In certain materials the phenomenon is persistent and, because

of its presence in alloys showing precipitation effects, it has usually been attributed to this factor; i.e., the decrease in length caused by the pre-

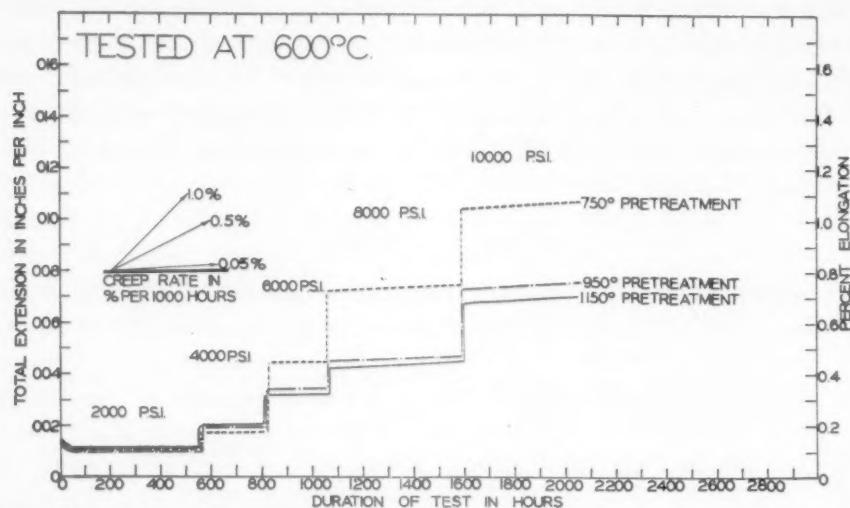


FIG. 1.—EFFECTS OF PRETREATMENT ON DEFORMATION CHARACTERISTICS AT 600°C. UNDER LOADS OF 2000, 4000, 6000, 8000 AND 10,000 POUNDS PER SQUARE INCH.

cipitation of a more dense compound out of the solid solution exceeds the extension caused by creep. The vacuum dilatometer used to check this point was similar to the one described by Walters and Gensamer.<sup>2</sup>

TABLE 1.—*Deformation Rates*  
PER CENT PER 1000 HOURS

Testing Temperature, Deg. C.	Load, Lb. per Sq. In.	Hours at Load	Cumulative Hours at Temperature	Series AM			Tests Previously Reported after 950°C. Pretreatment		
				Pretreatment at			Series AMK	Other 18-8 Alloys	
				1150°C.	750°C.	950°C.		Maximum	Minimum
600	2,000	555	555	<0.01	<0.01	<0.01	-0.02	<0.01	-0.02
600	4,000	262	817	<0.01	<0.01	<0.01	<0.01	0.09	<0.01
600	6,000	239	1,056	<0.01	<0.01	0.01	<0.01	0.19	<0.01
600	8,000	527	1,583	0.04	0.05	0.03	0.02	0.42	<0.01
600	10,000	467	2,050	0.04	0.05	0.03			
700	2,000	430	430	-0.025	0.01	0.01	-0.04	0.01	-0.04
700	4,000	581	1,011	0.02	0.02	0.05	0.05	0.15	0.05
700	6,000	456	1,467	0.17	0.11	0.31	0.35	0.80	0.25
700	8,000	431	1,898	1.52	1.73	3.28	2.25	2.90	0.86
800	2,000	426	426	0.09	0.14	0.17	0.26	0.26	0.26
800	4,000	526	952	1.69	4.93	4.83	0.80	3.0	0.80
800	6,000						24.0	44.5	10.0



The dilatometric curves gave a negative dilatation of the same order as the deformation curves; e.g., 0.0003 as against 0.0004 in. per in., indicating that the effect is independent of stress, and consequently that the precipitation explanation is probably the correct one, the extension due to creep being negligible under these conditions. The results also check those found in a previous attempt,<sup>1</sup> in which dilatation was studied in the deformation furnace itself under a "straightening" load of 100 lb. per sq. inch.

#### TESTS AT 700°C.

The results of the tests at 700°C. are shown graphically in Fig. 2. The differences in the deformation rates are much more noticeable than at the

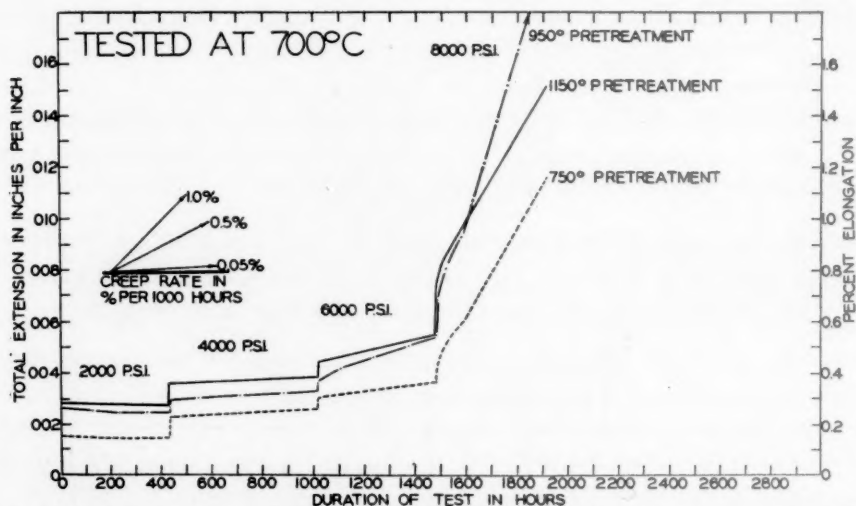


FIG. 2.—EFFECTS OF PRETREATMENT ON DEFORMATION CHARACTERISTICS AT 700°C. UNDER LOADS OF 2000, 4000, 6000 AND 8000 POUNDS PER SQUARE INCH.

lower temperature, as might be expected, and are appreciable for all stresses greater than 2000 lb. per sq. in. (Table 1).

In these tests, the specimen treated at 950°C. seems to be definitely inferior while between the other two there is not much choice. This is rather surprising because at first glance it would be anticipated that the specimens pretreated at 750°C. and 950°C. would give almost identical results because of their similar grain sizes. Furthermore, at this 700° test temperature, it would be expected that the rate of attainment of structural equilibrium would be fairly rapid and, consequently, that the temperature of pretreatment would have little effect other than that due to grain size.

Thus the results at this temperature indicate that the resistance to deformation is increased not only by the coarser grain size resulting from the higher pretreating temperature but also by the rapid initial precipitation of carbides at lower pretreating temperature.

While it is difficult to see from Fig. 2, because of the small scale, the initial negative creep at 2000 lb. per sq. in. has persisted, in the coarse-grained material, throughout the entire 430 hr. at load, while in the fine-grained specimens negative creep was completed after about 250 hr. at load. This is particularly puzzling, because at the lower test temperature the effect seemed to proceed to completion in a very much shorter time. However, surprising enough, no marked difference in rate of completion is noticeable between specimens pretreated at 750° and 950°C., where it most certainly would be expected. Since all three specimens behaved similarly at 600°C., it may be postulated that two precipitation reactions have to be considered: (1) a relatively rapid precipitation shown by all test bars at 600°C.; (2) a much slower precipitation at 700°C. It seems unreasonable to assume that the rapid initial negative creep observed in all specimens at 600°C. has not also occurred in all specimens when tested at 700°C. However, at the latter temperature it would be expected to occur even more rapidly, probably during loading, and to be masked completely by the initial plastic deformation during that stage.

As was found with the tests at 600°C., the agreement with the tests run previously was quite satisfactory, and was particularly good in the case of the specimen made by the same company.

#### TESTS AT 800°C.

The results of the tests at 800°C. are shown graphically in Fig. 3. Although only two loads were used the results are quite in conformity with what might have been predicted from the runs at 700°C. The data listed in Table 1 show that the material pretreated at high temperature is certainly superior. The other two specimens here gave similar results. As the curves show, the 750°C. specimen was somewhat superior at the 2000-lb. per sq. in. load, and for about 150 hr. of the 4000-lb. per sq. in. test, after which its deformation rate increased slowly, becoming almost identical with that of the 950°C. specimen after 375 hr. at 4000 lb. per sq. in. This indicates that even at 800°C. a period of nearly 800 hr. is required to get the two specimens into the same structural condition, the material partially precipitated during pretreatment being superior up to that point. With this in mind, it is not surprising that the results at 700°C. were unexpected. It is quite probable, as the deformation results

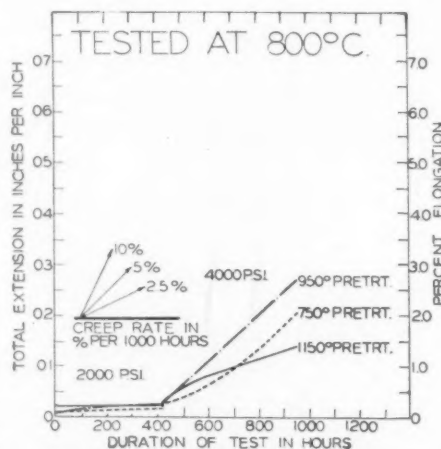


FIG. 3.—EFFECTS OF PRETREATMENT ON DEFORMATION CHARACTERISTICS AT 800°C. UNDER LOADS OF 2000 AND 4000 POUNDS PER SQUARE INCH.

suggest, that the specimens never became similar within the 1900 hr. of the test.

The general tendency in 18-8 steels, as well as in many other materials, of coarse-grained specimens to give lower deformation rates as the temperature of recrystallization is exceeded is, of course, well known.<sup>3</sup> The

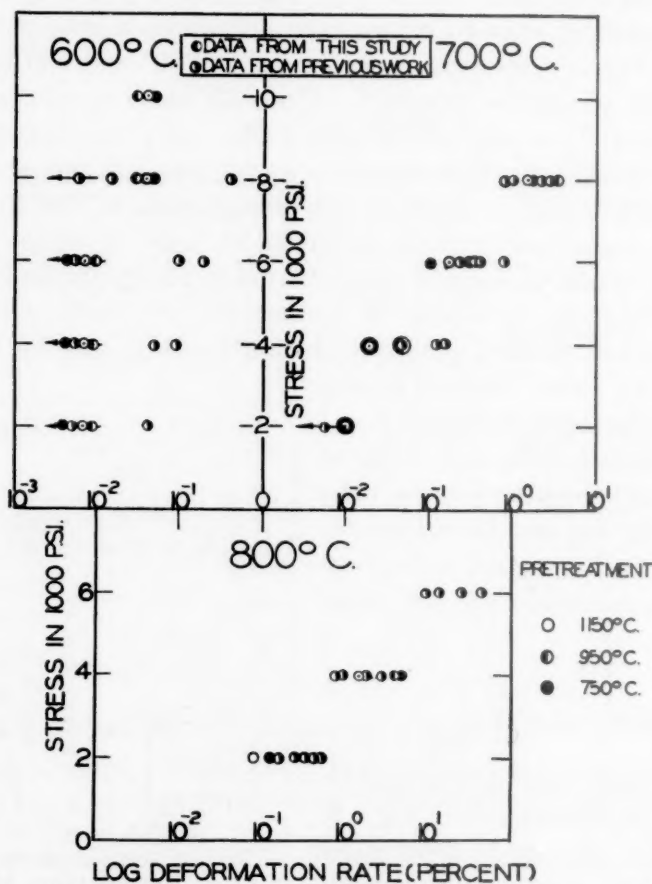


FIG. 4.—PLOTS OF STRESS VS. LOG DEFORMATION RATE FOR TESTS AT 600°, 700° AND 800°C.

researches of French, Kahlbaum, and Peterson<sup>4</sup> and of Kanter and Spring<sup>5</sup> may also be cited.

However, the means found in the present work of strengthening the fine-grained material by partial precipitation of the dissolved carbides before testing does not seem to have been reported previously in the literature.

Fig. 4 is a plot, using coordinates of stress vs. log secondary creep rate, of the data secured at the three test temperatures. Also shown are the results of previous work done with the same equipment on steels of similar chemical composition.

## METALLOGRAPHY

Comprehensive metallographic studies were made on the test bars for the purpose of examining the effect of stress at elevated temperatures on the structure; and to determine what correlation might obtain between the relatively small differences in creep behavior, after different pretreatments, and the changes in microstructure of the stainless steels. In general, the specimens were examined after the completion of the test both in the gauge length and in the portion of the larger shank, which was in the constant-temperature zone throughout the test, as shown in Fig. 5. Both the transverse and the longitudinal sections of these specimens were examined and no appreciable differences were noted. Accompanying the creep specimens unstressed pieces of the same material were suspended in the furnace under identical conditions, and from these, at periodic intervals corresponding to the times at which the load was changed, pieces were cut and examined to determine the effects of time alone on the microstructure. A comparison of the gauge, hot shank, and unstressed specimens gave, therefore, information with respect to the effects of stress and its accompanying plastic deformation upon the microstructure. Examination of 100 dia. served to disclose any variation in grain size, while a magnification of 750 dia. seemed to suffice for a satisfactory study of the nature and form of the carbide precipitate.

Figs. 6 to 14 show the structures in the as-received condition, and after air quenching following 15 min. in hydrogen at 1150°, 950°, and 750°C. Since the as-received condition represented a manufacturer's anneal at 1066°C., it would not be expected that the grain size would be affected by subsequent treatment at a lower temperature. The indications, however, were that 1066°C. was within the so-called "coarsening range," so that a mixed grain size resulted. The material treated at 1150°C., on the other hand, had a grain size roughly eight times as large.

Figs. 10 to 14 show the effects of pretreatment on the precipitated carbides. The solvus for the carbides falls within the range 937° to 950°C.; i.e., a specimen treated at the former temperature showed coarse grain-boundary precipitate (Fig. 13), while one treated at the latter temperature had the carbides completely in solution (Fig. 12). The material treated at 750°C. also had carbides at the grain boundaries but

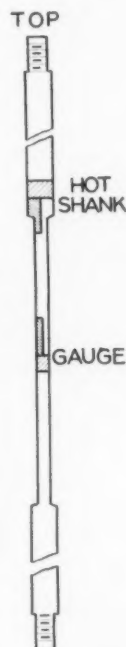
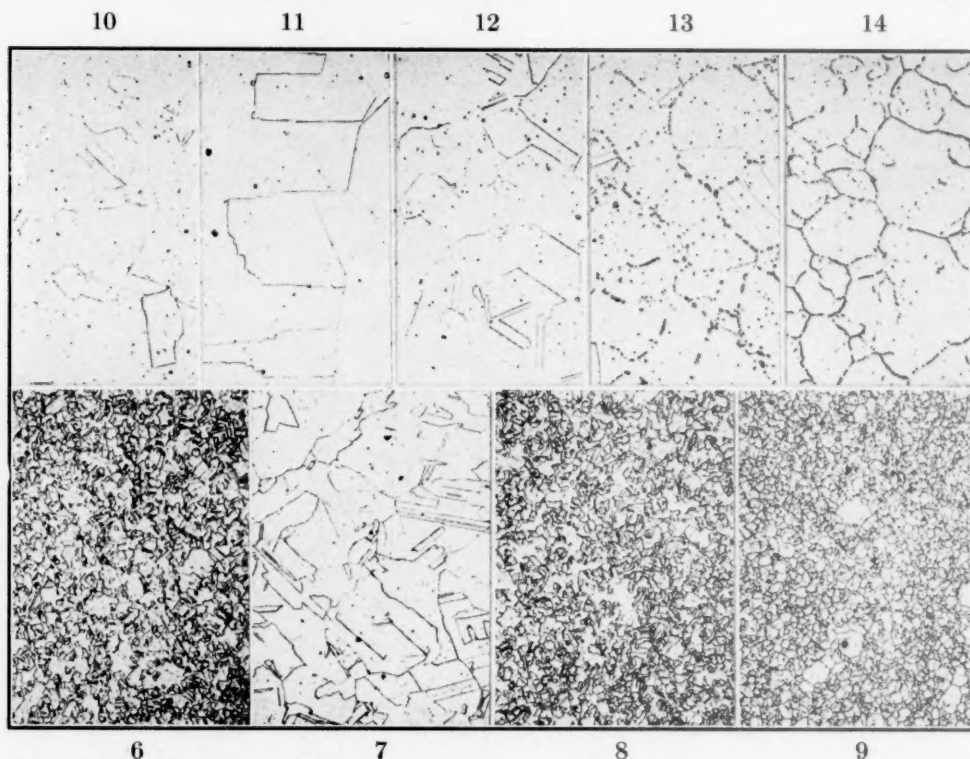


FIG. 5.—SECTION OF DEFORMATION SPECIMENS SHOWING LOCATIONS STUDIED METALLOGRAPHICALLY.



they were much finer than those precipitated at the higher temperature. As mentioned previously, therefore, a comparison of the 1150° and the 950° pretreatments (Figs. 7 and 8) permits a determination of the effects of grain size when both alloys are single phase initially, while a comparison



FIGS 6-14.—EFFECTS OF TEMPERATURE OF PRETREATMENT ON GRAIN SIZE AND CARBIDE PRECIPITATION IN AN 18-8 STAINLESS STEEL.

Fig. 6.—As received (mill anneal at 1066°C. (1950°F.) followed by an air cool.  $\times 100$ .

Fig. 7.—Heated 15 minutes in hydrogen at 1150°C. (2100°F.) and air-cooled.  $\times 100$ .

Fig. 8.—Heated 15 minutes in hydrogen at 950°C. (1740°F.) and air-cooled.  $\times 100$ .

Fig. 9.—Heated 15 minutes in hydrogen at 750°C. (1380°F.) and air-cooled.  $\times 100$ .

Fig. 10.—Same as Fig. 6, showing freedom from carbide precipitation.  $\times 750$ .

Fig. 11.—Same as Fig. 7, showing increase in grain size and freedom from carbide precipitation.  $\times 750$ .

Fig. 12.—Same as Fig. 8.  $\times 750$ .

Fig. 13.—Heated 15 minutes in hydrogen at  $937 \pm 5^\circ\text{C}$ . and air-cooled, showing coarse particles of carbide precipitated apparently by heating just under the solvus temperature.  $\times 750$ .

Fig. 14.—Same as Fig. 9, showing character of carbide precipitation.

Etched electrolytically in a 2.5 per cent oxalic acid solution.

Original magnifications given; reduced approximately  $\frac{1}{2}$  in reproduction.

of the 950° and 750° pretreatments (Figs. 8 and 9) permits a determination of the effects of initial precipitation when both alloys are of the same grain size originally.

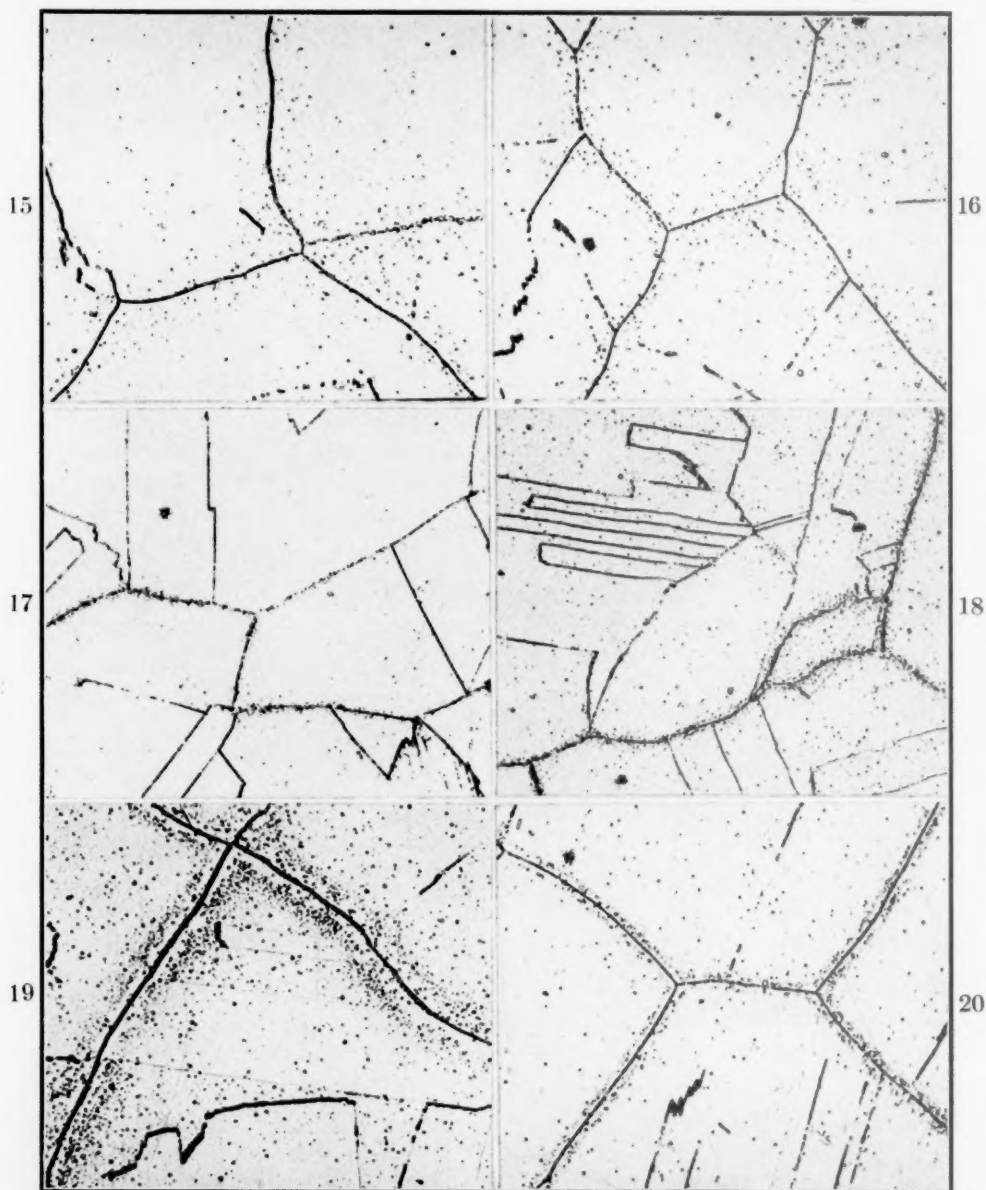
No appreciable change in grain size as a result of testing was found in either the stressed or unstressed material.

## EFFECTS OF TESTS UPON FORM AND MANNER OF CARBIDE PRECIPITATION

The microstructure of the specimens that were pretreated at 1150°C. provided the greater amount of information because of their larger grain size. The untested material (Fig. 11), as noted previously, showed only the usual twinned austenitic structure. When this was heated, unstressed, at 600°C. for varying times the structures shown in Figs. 15, 16, 17 and 18 were produced, the last one representing 2280 hr. at temperature. It will readily be seen that, even after this interval, the amount of precipitate was apparently still increasing. The rate of carbide precipitation at this temperature is a very slow process. It was also noticed that, where precipitation did occur, the locations preferred, in chronological order, were: (1) grain boundaries; (2) ends of internal twins; (3) sides of internal twin bands; and (4) within the grains. This is perhaps not shown as well as could be desired but was amply confirmed by observation.

Considering next the test samples subjected to strain at 600°C., Fig. 19, taken from the hot shank section, shows the effect of stresses of the order of 320 to 1600 lb. per sq. in. upon the structure, while Fig. 20, taken from the gauge section, shows the effects of stresses increased from 2000 to 10,000 lb. per sq. in. at the time intervals shown in Fig. 1. The same general phenomena obtain. The heaviest precipitate is formed at the grain boundaries and at the ends of internal twins, while only in a few sections has any precipitation occurred at the sides of the twin bands or within the grains. However, an entirely distinct type of grain-boundary precipitation is found in these two specimens, the precipitate being found not only in the boundary but also in a "cloud" somewhat removed from the boundary. It is difficult to explain this peculiarity. While it seems obvious that it should be attributable in some manner to the applied stress, since it is lacking in the unstressed specimen (Fig. 18, specimen heated, unstressed, for a comparable time), still the effect was not observed in other specimens that were heated for only about 1000 hr. at 600°C. under comparable stresses. Another observation also makes it appear that stress alone is only a contributory factor. The precipitation of this type was much more marked near the surface of the specimen and decreased progressively toward the center. This may or may not be significant, but it does suggest the possibility of some complications due to the penetration of oxygen or nitrogen.

The effects of heating, unstressed, at 700°C. can be seen by comparing Figs. 21, 22, 23 and 24 with Fig. 11, the longest time of treatment shown being 1940 hr. The same general phenomena observed at 600°C. are found here. The precipitate also is much coarser and better developed, as would be anticipated from the higher test temperature. A different form of precipitate is especially prominent here. Although it was also found at the lower temperature, it was not mentioned specifically because



FIGS. 15-20.—EFFECT OF TIME AT 600°C. (1110°F.) AND OF STRESS CONDITIONS ON CARBIDE PRECIPITATION IN SPECIMENS PRETREATED AT 1150°C. (2100°F.)  $\times 750$ .

Fig. 15.—Heated for 690 hours, unstressed.

Fig. 16.—Heated for 960 hours, unstressed.

Fig. 17.—Heated for 1770 hours, unstressed.

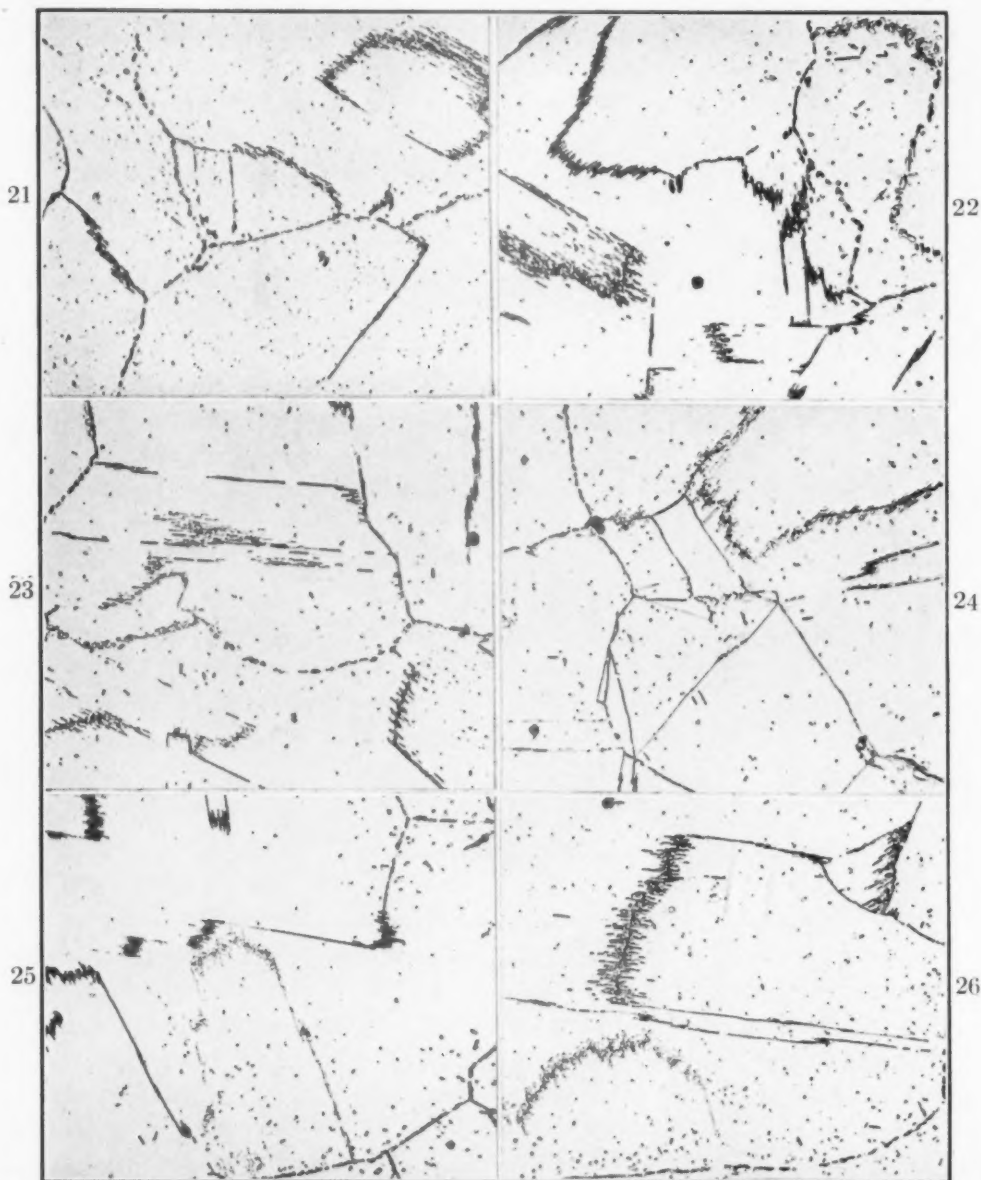
Fig. 18.—Heated for 2280 hours, unstressed.

Fig. 19.—Heated for 2050 hours under stresses of 320 to 1600 lb. per sq. in. Specimen AM1. Hot shank section.

Fig. 20.—Heated for 2050 hours under stresses of 2000 to 10,000 lb. per sq. in. Specimen AM1. Gauge section.

Etched electrolytically in 2.5 per cent oxalic acid solution.

Original magnification given; reduced  $\frac{1}{3}$  in reproduction.



FIGS 21-26.—EFFECT OF TIME AT 700°C. (1290°F) AND OF STRESS CONDITIONS ON CARBIDE PRECIPITATION IN SPECIMENS PRETREATED AT 1150°C. (2100°F.).  $\times 750$ .

Fig. 21.—Heated for 457 hours, unstressed.

Fig. 22.—Heated for 863 hours, unstressed.

Fig. 23.—Heated for 1504 hours, unstressed.

Fig. 24.—Heated for 1940 hours, unstressed.

Fig. 25.—Heated for 1898 hours under stresses of 320 to 1280 lb. per sq. in. Specimen AM2. Hot shank section.

Fig. 26.—Heated for 1898 hours under stresses of 2000 to 8000 lb. per sq. in. Specimen AM2. Gauge section.

Etched electrolytically in 2.5 per cent oxalic acid solution.

Original magnification given; reduced  $\frac{1}{3}$  in reproduction.



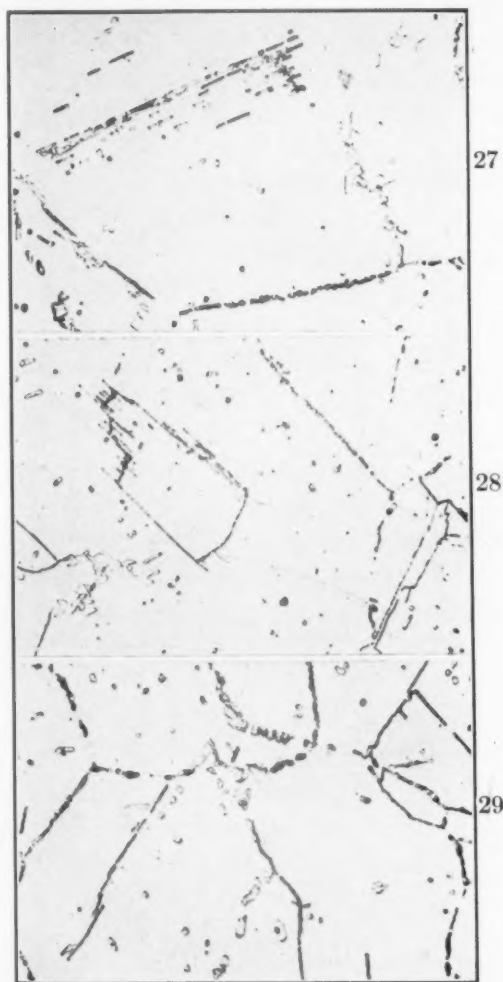
of its meager character. The edges of internal twin bands in particular, and in a few cases the curved sides of twins and sections of grain boundaries, show a very ragged type of precipitate, which extends in nearly parallel lines into the areas on either side of the boundary. The parallel nature of the particles suggests strongly a connection with some crystallographic mechanism.

From a comparison of Figs. 24, 25 and 26, which show, respectively, material unstressed, stressed at 320 to 1280 lb. per sq. in. and stressed at 2000 to 8000 lb. per sq. in. at 700°C., it can be seen that stress apparently has had little effect on the structures produced. It is to be noted that no trace of the peculiar type of grain-boundary precipitation found at the lower temperature was detected in these specimens.

The tests at 800°C., because of the lower strength of the alloy, were much more limited in scope. Fig. 27 shows the structure of the material after heating, unstressed, for 960 hr. After a similar time at temperature the results of stresses of 320 and then 640 lb. per sq. in. on the hot shank and of stresses of 2000 and then 4000 lb. per sq. in. on the gauge section are shown in Figs. 28 and 29, respectively. The precipitate was, naturally very much coarser; and, although it occurred in the same general position as at the lower temperatures, there was apparently less of it because of the greater degree of agglomeration. There also appeared to be, in these specimens particularly, although the same effect was noted at the lower temperatures, two distinct types of precipitate. One of these, etching usually somewhat darker and occurring predominantly at grain boundaries and along twin bands, is believed to be a form of carbide. The other, usually etching light and clear or somewhat pinkish in color, is probably ferritic in nature. It seemed to occur in some specimens in the vicinity of grain boundaries, as with the plates in the right edge of Fig. 27, the lower corner of Fig. 28, and the central part of Fig. 29. In other specimens its relationship seemed to be closest to the sides of twin bands, although for the two bands shown in the right central portion of Fig. 28 even this seems doubtful. Austin and Nickol<sup>1</sup> reported somewhat similar "needles" in their work but in some respects even these seem to be of a different nature, the pinkish tinge of the particles, in particular, being much more marked in their specimens.

No detailed discussion is presented of the microstructures of the steel pretreated at 950° and 750°C. Because of the smaller grain size of these specimens and the consequent more crowded nature of the structure, it was difficult to select characteristics of note. It was observed that for both these pretreatments the amount of precipitate after testing at 600°C. was still apparently increasing even after the longest time studied, 2280 hr. The general locations at which precipitate occurred preferentially also seemed to be the same as in the coarser-grained steel, but the

peculiar "divorced" type of precipitate (remote from grain boundary) found in the coarser-grained material did not seem to occur.



FIGS. 27-29.—EFFECT OF TIME AT 800°C. (1470°F.) AND OF STRESS CONDITIONS ON CARBIDE PRECIPITATION IN SPECIMENS PRETREATED AT 1150°C.  $\times 750$ .

Fig. 27.—Heated for 960 hours, unstressed.

Fig. 28.—Heated for 960 hours under stresses of 320 and 640 lb. per sq. in. Specimen AM3. Hot shank section.

Fig. 29.—Heated for 960 hours, under stresses of 2000 and 4000 lb. per sq. in. Specimen AM3. Gauge section.

Etched electrolytically in 2.5 per cent oxalic acid solution.

Original magnification given; reduced  $\frac{1}{3}$  in reproduction.

The higher test temperature of 700°C. seemed only to cause a coarser precipitate and produced no major differences between the 750° or 950°C. pretreatments.

For the specimens tested for 960 hr. at 800°C., little comment can be made. Stress had no apparent effect at this temperature either on the character or the degree of agglomeration of the precipitate.

## GENERAL COMMENTS

The primary purpose of the investigation was to study the effect of temperature of pretreatment of 18-8 stainless steels on their behavior under tensile deformation at 600°, 700°, and 800°C.

Considering first the tests at 600°C., for a common time at temperature and set of stress conditions it was found that (1) the size of precipitate and (2) the distance from the grain boundaries at which the "cloud-like" precipitate occurred was practically the same for each of the three pretreatments. This indicates, as might be expected, that both the precipitation and the agglomeration are dependent upon test temperature, and are independent of the grain size of the steel. The rate of diffusion of one of the major elements is probably the determining factor.

It has been shown also that modification of the alloy pretreatment has little effect on creep characteristics.

On testing at 700°C. the amount of grain-boundary precipitate seemed to be about the same for each of the three differently pretreated specimens. The coarse-grained material, however, had much more precipitate within the grains, concentrated largely along internal twin bands. The differences between the two fine-grained materials were slight. Under these conditions it is difficult to explain the results of the deformation tests except on the basis previously mentioned; namely, the strengthening effect of fine precipitate formed by the 750° pretreatment. The superiority of the steel pretreated at 1150° over that treated at 950°C. is undoubtedly due to its larger grain size, since the two specimens were otherwise in the same initial condition.

Finally, a comparison of the three differently pretreated steels, on testing at 800°C. showed no major difference either in their resistance to deformation or change in microstructure.

The more important results of the investigation may be summarized as follows:

1. Confirming the results of previous investigators, an increase in grain size is found to increase the resistance to deformation of 18-8 stainless steels only at the higher test temperatures.

2. The temperature above which increased grain size becomes effective lies between 600° and 700°C., and is probably associated with progressive recrystallization, as pointed out by White and Clark.<sup>3</sup>

3. On testing at a temperature below that at which recrystallization becomes effective (600°C.), no evidence has been obtained to show that temperature of pretreatment has any material effect on creep characteristics of the alloy.

4. Evidence has been presented to indicate that the advantage provided by coarse grains, on testing at 700°C., may be substituted by a heat-treatment that results in the formation of a fine precipitate within

the fine-grained steel. The strengthening effect of this precipitate appears to persist for at least 2000 hr. Higher test temperatures presumably lead to agglomeration and concomitant decrease in resistance to deformation in 600 to 800 hours.

5. At 600° and 700°C. the precipitation process associated with stainless 18-8 steel is a relatively slow one and apparently proceeds for several thousand hours.

6. Precipitation seems to occur, preferentially, in the following locations: (a) grain boundaries; (b) ends of annealing twin bands; (c) sides of annealing twin bands; and (d) within the grain.

7. Two types of precipitate occur, one of which is probably carbide while the other, slightly pinkish in color, is probably ferritic in nature.

8. Neither stress nor the plastic deformation accompanying it, in the range studied, seemed to have any effect on the character of the carbide precipitate.

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#### DISCUSSION

(R. H. Aborn presiding)

E. S. DAVENPORT,\* Kearny, N. J.—I am somewhat puzzled by the authors' use of the term "recrystallization" in conclusion 3. I have always been under the impression that "recrystallization" implied the formation of new grains from a cold-worked structure when the latter was appropriately heated.

E. P. POLUSHKIN,† New York, N. Y.—Figs. 19 and 20 show a large mass of carbides at a distance from the boundaries of grains. Can the authors explain why the precipitation of carbides did not occur directly at the boundaries of the grains, as usually happens?

J. T. MACKENZIE,‡ Birmingham, Ala.—The authors mentioned rods and plates in the structure. Did they arrive at this from the two-dimensional pattern shown in the

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photomicrographs or did they establish the three-dimensional formation by the method of successive polishing and photographing?

C. R. AUSTIN AND C. H. SAMANS (authors' reply).—Our use of the term "recrystallization" in conclusion 3 is quite possibly open to question, as Dr. Davenport points out. Since so little is known concerning the exact mechanism of recrystallization the range of phenomena that fall within its scope cannot very well be decided at this time. However, while we know little about recrystallization, we know still less about the so-called "equicohesive" temperature, although some investigators have claimed the two to be synonymous. In the selection of the term "recrystallization" in preference to "equicohesive," our intention is to signify some temperature above which the application of strain and its removal occur simultaneously and below which the removal of strain is very much slower, so that the alloy is strengthened to some extent. There was no definite evidence of recrystallization in these specimens in the accepted sense, and we certainly doubt that any occurred because the deformations were too minute.

We regret that we do not possess sufficient information regarding the precipitate that we have designated as "carbides" to throw much light on Mr. Polushkin's question. A purely speculative explanation can be given, but only further study, which we did not feel was justified, can determine its worth. The first precipitation of grain-boundary carbides apparently forms and agglomerates in the boundary itself, and, in addition, impoverishes an appreciable area on either side in both carbon and chromium. This seems to be the accepted theory. Since carbon diffuses more rapidly than chromium, enrichment in this element will take place, with time, more rapidly than that with chromium. Consequently, the subsequent precipitation will occur at some point away from the boundary where both the carbon and the chromium have attained the correct concentration. The region between will contain no precipitate. On the other hand, since this type of precipitate seems to be the exception instead of the rule, it may be due entirely to some special set of conditions, accidentally obtaining, and concerning which we cannot even speculate.

The point raised by Dr. MacKenzie also cannot be answered definitely because we did not feel that the results would justify the time required. Our description of the particles as "rods" or "plates" was based entirely on examination, metallographically, of their appearance in numerous sections similar to those shown.

## A New Instrument for the Magnetic Determination of Carbon in a Steel Bath

BY H. K. WORK,\* MEMBER A.I.M.E., AND H. T. CLARK†

(Chicago Meeting, October 1939)

THE instrument for the rapid determination of carbon in steel, described in this paper, was developed originally to facilitate the operation of the pilot-sized open-hearth furnace in the Jones & Laughlin Research and Development Laboratory. In this small furnace, with its shallow bath, the drop in carbon is accelerated, and a rapid, reliable test for carbon content is indispensable. This problem becomes rather acute when it is desired to finish heats at a carbon content higher than can be estimated with any degree of accuracy by the fracture test. Several independent methods for determining carbon were investigated, therefore, and it was found that a relatively simple magnetic device could be made to give reproducible results. A laboratory instrument was designed and set up for the use of the furnace operators. It was tested exhaustively in the laboratory and was used with considerable success for following the carbon content in the furnace bath. As soon as sufficient data had been compiled to indicate that the instrument might have a wider application, a more rugged model was constructed and placed in the mill to be tested on commercial heats. Finally, about a year ago, instruments were furnished to the plant open-hearth shops, and these have been in use since that time. As a matter of convenience, the instrument has been named the "Carbanalyzer," and will be referred to by this designation in the following pages.‡

### EARLIER INVESTIGATIONS

While by far the greatest number of magnetic investigations in which the carbon content of ferromagnetic materials was considered have had to do with the evaluation of the magnetic properties of steels of known

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Manuscript received at the office of the Institute July 31, 1939. Issued as T.P. 1132 in METALS TECHNOLOGY, December 1939.

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‡ Certain features of the Carbanalyzer are the subject of patent applications, and arrangements have been made with the Fisher Scientific Co. of Pittsburgh to make the instrument generally available to the industry.

analysis, several investigators have considered the problem of evaluating carbon content by one or another of the magnetic properties. Of considerable historical interest is the work of the Reverend William Scoresby<sup>1</sup> who, in 1839, recorded some attempts to determine the carbon content of steel by measuring the retentivity of a magnetized specimen, and that of C. M. Ryder,<sup>2</sup> who described an instrument for the same purpose in the *TRANSACTIONS* of the A.I.M.E. for 1876.

During the last 20 years of the last century, various instruments were developed for measuring accurately the magnetic properties of transformer steel and similar materials, and thought was given to the relationship between these properties and carbon content of the materials. Two consecutive articles on the subject appear in the 1896 volume of the *Minutes of the Proceedings of the Institution of Civil Engineers*.<sup>3,4</sup> The former of these described the equipment necessary for obtaining the permeability of steel specimens, while the latter gave flux densities, at various magnetizing forces, for steels of from 0.17 to 0.70 per cent carbon. Madame Curie,<sup>5</sup> two years later, showed definitely that the flux through a hardened steel specimen is related to the carbon content, at a fixed magnetizing force.

More recently three magnetic methods for rapid evaluation of carbon content in steel have been developed. The first of these is embodied in the carbometer of Malmberg,<sup>6-9</sup> the second in the Bureau of Mines coercimeter<sup>10</sup> and the third is a comparison method developed by Blosjo.<sup>11</sup> The carbometer, in principle, resembles a permeameter except that the change in flux in the specimen is produced by a mechanical arrangement involving the use of a permanent magnet and rotating soft-steel bars. A cam mechanism within the instrument produces a set number of reversals of flux in order to put the specimen in a standard state, and completes the galvanometer circuit only for the final change in flux, which produces the reading. By this arrangement, the ballistic galvanometer receives a single impulse. The coercimeter makes use of another magnetic property—the coercive force—which has been defined as “the intensity of the magnetic field that must be applied in the direction opposite to that in which the specimen was originally magnetized to reduce the magnetic flux to zero.” The procedure, briefly, consists in magnetizing the specimen in a powerful electromagnet, then transferring it to a calibrated solenoid coil, and measuring the current in the coil necessary to reduce the magnetic field of the specimen to zero. Blosjo’s method depends on the change in permeability with change in carbon content, and compares the test specimen with a standard bar of about 0.21 per cent carbon. It is essentially a null method except that the small readings for unbalanced samples are used for calibration.

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<sup>1</sup> References are at the end of the paper.

## GENERAL CONSIDERATIONS

Various methods by which the fundamental magnetic quantities may be measured have been known for many years and are described in the literature on the subject. The Carbanalyzer may be considered as a special form of a permeameter, since it measures the change in flux in a bar produced by a known change in magnetizing force. The change in the magnetizing force ( $\Delta H$ ) in this case is equal to  $2H$  and the change in flux ( $\Delta \phi$ ) is equal to  $2\phi$ , because the current in the magnetizing coil is reversed. Therefore, if the cross-sectional area of the bar specimen is known, it is possible to calculate the permeability of the material, for the known value of  $H$ , by the application of the ordinary magnetic equations.

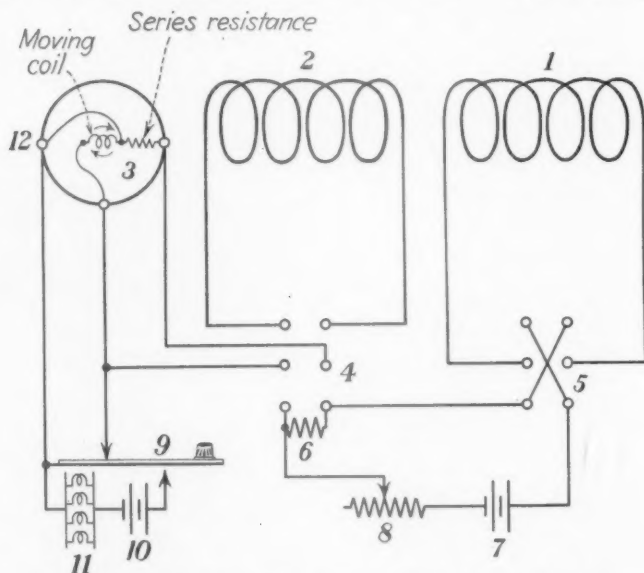


FIG. 1.—ELECTRICAL CIRCUIT OF THE CARBANALYZER.

The absolute value of the various quantities are of no interest in the present application; attention is paid solely to galvanometer deflections for a reversal of a given magnetizing current, and these deflections are calibrated in terms of carbon content. The main objectives in this work have been: (1) accuracy and reproducibility of results, (2) ease and speed of operation, and (3) simplicity and ruggedness of equipment.

## CONSTRUCTION DETAILS

The details of the electrical circuit of the Carbanalyzer are shown in Fig. 1. Coils 1 and 2 are the primary and secondary of a special induction coil. The current in the primary coil is supplied by battery 7, measured by meter 3, controlled by rheostat 8, and reversed by switch 5. The other double-pole, double-throw switch 4 is inserted in order that the same meter may be used in both the primary circuit (in parallel



with the resistance 6) to measure the steady current, and in the secondary circuit as a ballistic instrument. The meter is a millivoltmeter and is designed to be short-circuited when not in use to prevent damage to the moving parts. This feature is used to advantage; the meter is short-circuited to protect it during the several reversals of current necessary to put the specimen in a standard state. The push-button switch 9 in its normal position short-circuits the meter through the shorting terminal 12. When pushed down for a reading, it releases the meter and lights, by means of battery 10, a group of flashlight bulbs 11 above the meter scale.

The millivoltmeter has a fairly rapid motion when used as a ballistic instrument, but has been used advisedly since it is satisfactory in a portable machine and may be read accurately by the aid of a small two-power reading glass mounted above the meter face. Likewise, it does not require leveling, holds its zero setting well, and is not affected by any normal mill vibration. Other electrical parts, with the exception of the magnetic unit, are standard equipment.

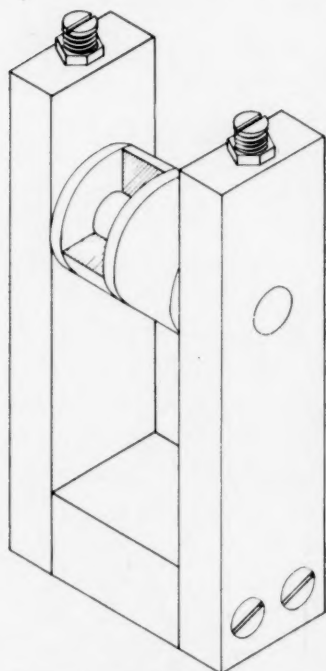


FIG. 2.—THE MAGNETIC UNIT.

The magnetic unit is shown in Fig. 2. The primary and secondary coils are wound on a hollow Bakelite form and held in position between the two heavy steel plates forming the sides of the yoke. The cylindrical specimen is thrust through the holes in the yoke and the coils, and is held in good magnetic contact with the yoke. This is a closed magnetic circuit, and stray magnetic fields in the vicinity cause no difficulty. The specimen may be inserted and withdrawn readily and will always be held in the same position with the same sidewise thrust against the soft-steel yoke. It has been amply demonstrated in repeated tests on the same specimen that the readings are reproducible, showing that the same magnetic coupling is attained each time the specimen is inserted. The size and shape of the specimen may be varied through relatively wide limits, although care must be taken that only specimens of the type for which the machine was calibrated are used.

One machine may be required to follow at the same time two or more heats with very different carbon contents, and it was considered desirable to use a single setting for both the high range and low range of carbon content. The Carbanalyzer has been so designed that it is possible for readings to be taken on high-carbon and low-carbon samples alternately with no change in the instrument. The deflections do not overlap and

there is no possibility of confusion. At the same time the accuracy, in terms of carbon content, has been found to be quite satisfactory.

An assembled Carbanalyzer is shown in Fig. 3. This model is approximately 10 by 10 by 14 in. and weighs 30 lb. The batteries are in a special compartment in the base, so that the unit is completely self-contained and portable.

#### PREPARATION OF SPECIMEN

The original experimental work included a study of the magnetic characteristics of specimens quenched under various conditions. It was



FIG. 3.—THE FISHER CARBANALYZER.

found that a delayed quench was satisfactory for steels with carbon content below about 0.40 per cent, but that for carbons higher than that the readings were not selective. A rapid quench was then tested for the range from 0.20 up to 1.50 per cent carbon, and the results indicated that this method gave selective values from 0.35 per cent carbon up to 1.50 per cent or higher. The following procedure was adopted: a sample of metal was taken from the bath, killed with a measured quantity of aluminum and cast in a split mold. The specimen was removed from

the mold and quenched immediately for higher carbon contents, or left in the mold for a predetermined time—one minute—and then cooled in cold water, for the low-carbon steels. For steels that were known to contain from 0.30 to 0.50 per cent carbon, but where the amount was known only approximately, a sample was taken following each procedure and the appropriate range and the carbon value determined from the two

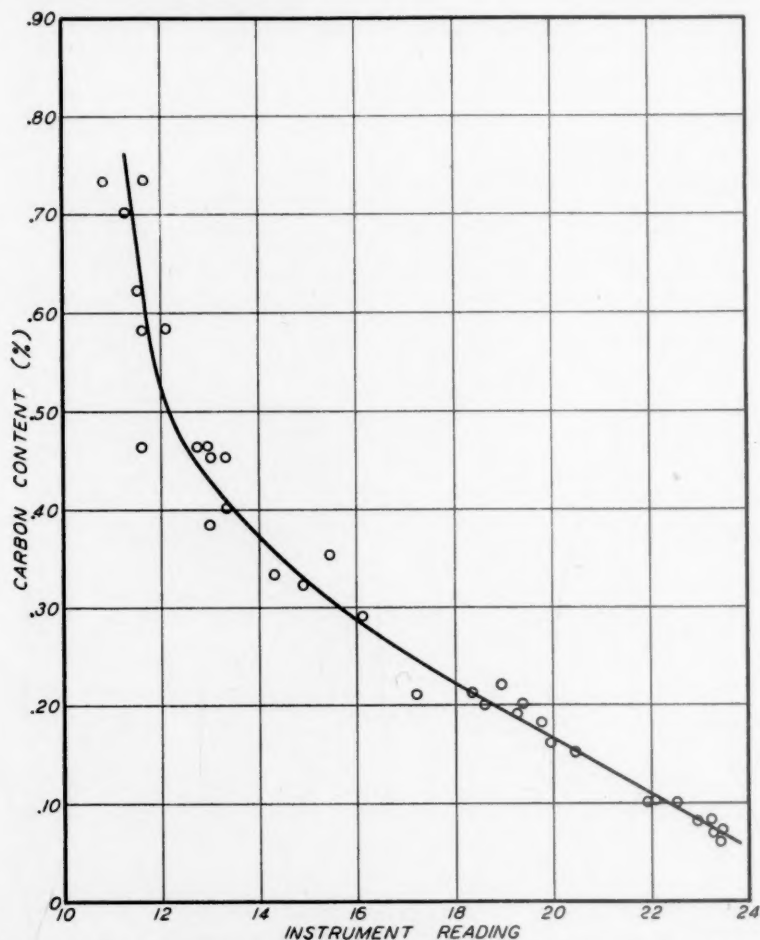


FIG. 4.—CALIBRATION CURVE OF ORIGINAL LABORATORY INSTRUMENT.

readings. It was standard practice to break each sample after the reading had been taken in order to be certain that the internal structure was sound.

#### PERFORMANCE OF CARBANALYZER

Samples were taken on the early laboratory heats and tests run on the laboratory instrument. These samples were taken at various stages of the heat and were later analyzed for carbon content. The relationship between the readings and carbon content is shown graphically in Fig. 4. The samples were all delay-quenched, and it may be seen that, as has been mentioned, the results are not satisfactory above 0.40 per cent

carbon. The relationship shown here is in general satisfactory, but it is not as good as was obtained later with a more refined instrument. A portable model was built in the laboratory and taken to the mill where, with the cooperation of the mill people, results were obtained much more rapidly than would have been possible in the laboratory. This early mill work was valuable also because it suggested several minor changes in design that were desirable so that accurate readings might be obtained

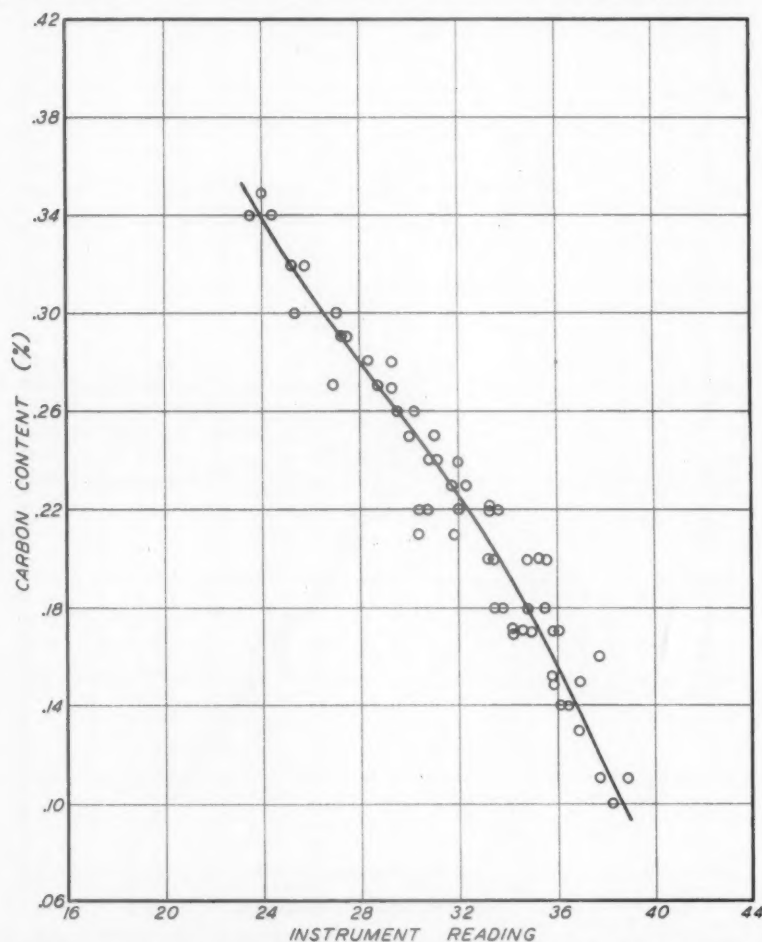


FIG. 5.—CALIBRATION CURVE OF A MILL INSTRUMENT FOR THE LOW-CARBON RANGE.

consistently. During and at the end of this mill trial a careful search was made for possible improvements.

This study resulted in the Carbanalyzer in its present form. The magnetic unit shown in Fig. 2 was designed to provide uniform magnetic coupling between the specimen and the yoke, and to require a very small current from the dry cells for its operation. Certain other minor changes were made at the same time. The procedure described above, however, was used for preparation of the specimens. One of these new instruments was then placed in each of the company's mills, and was calibrated there.



Reports have been favorable and the Carbanalyzers have met the requirements of the operators.

The graphs of Figs. 5 to 7 are included to show the results obtained on the mill instruments with samples made from commercial heats of steel. This information came to the laboratory in reports from the mill and has been assembled for presentation in this paper. Table 1 shows a

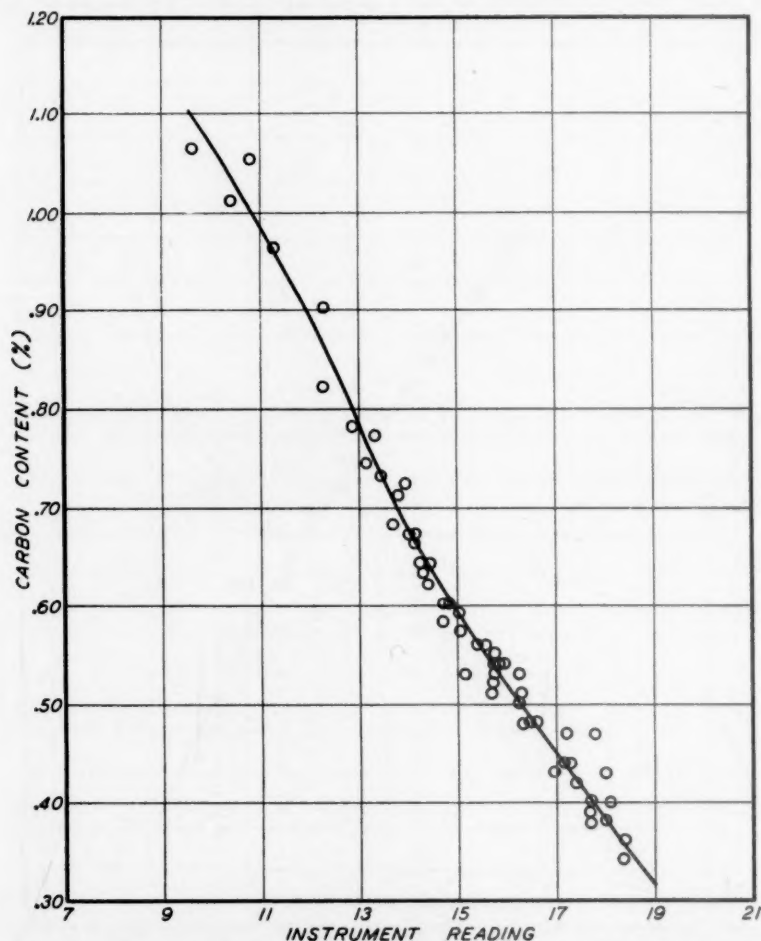


FIG. 6.—CALIBRATION CURVE OF A MILL INSTRUMENT FOR THE HIGH-CARBON RANGE.

series of these data, while Figs. 5 and 6 show the curves of readings against carbon content, as determined by the combustion method, for the low and high carbon ranges. Fig. 7 shows these same data in the form of a frequency-deviation graph with the deviation expressed in units of 0.01 per cent carbon and the frequency in number of samples; 94 of the 112 samples were within  $\pm 0.02$  per cent carbon of the value by the analytical method. Similar information on the other Carbanalyzers in the mills has been compiled and presents substantially the same story. It is obvious that the curves would be shifted for steels containing nickel, chromium,

TABLE 1.—Carbon Values as Determined by Carbanalyzer Compared with Analyses by Combustion Method

Low Range				High Range			
Reading	Carbon by Carbanalyzer	Carbon by Combustion	Deviation	Reading	Carbon by Carbanalyzer	Carbon by Combustion	Deviation
38.2	0.11	0.10	+0.01	18.3	0.35	0.34	+0.01
37.6	0.12	0.11	+0.01	18.3	0.35	0.36	-0.01
38.9	0.09	0.11	-0.02	17.9	0.38	0.38	0.00
36.9	0.13	0.13	0.00	17.6	0.40	0.38	+0.02
36.1	0.15	0.14	+0.01	17.6	0.40	0.39	+0.01
36.4	0.14	0.14	0.00	17.6	0.40	0.40	0.00
35.8	0.15	0.15	0.00	18.0	0.37	0.40	-0.03
35.8	0.15	0.15	0.00	17.3	0.42	0.42	0.00
36.9	0.13	0.15	-0.02	17.9	0.38	0.43	-0.05
37.7	0.12	0.16	-0.04	16.9	0.45	0.43	+0.02
36.0	0.15	0.17	-0.02	17.1	0.44	0.44	0.00
35.7	0.16	0.17	-0.01	17.2	0.44	0.44	0.00
34.9	0.17	0.17	0.00	17.1	0.44	0.47	-0.03
34.5	0.18	0.17	+0.01	17.7	0.40	0.47	-0.07
34.2	0.19	0.17	+0.02	16.5	0.48	0.48	0.00
34.2	0.19	0.17	+0.02	16.4	0.48	0.48	0.00
33.5	0.20	0.18	+0.02	16.3	0.49	0.48	+0.01
33.8	0.19	0.18	+0.01	16.2	0.50	0.50	0.00
34.9	0.17	0.18	-0.01	16.2	0.50	0.51	-0.01
35.5	0.16	0.18	-0.02	15.6	0.54	0.51	+0.03
33.2	0.20	0.20	0.00	15.7	0.53	0.52	+0.01
33.5	0.20	0.20	0.00	15.7	0.53	0.53	0.00
34.8	0.17	0.20	-0.03	16.2	0.50	0.53	-0.03
35.2	0.17	0.20	-0.03	15.1	0.57	0.53	+0.04
35.4	0.16	0.20	-0.04	15.7	0.53	0.54	-0.01
30.4	0.24	0.21	+0.03	15.8	0.53	0.54	-0.01
31.8	0.22	0.21	+0.01	15.9	0.52	0.54	-0.02
30.4	0.24	0.22	+0.02	15.7	0.53	0.55	-0.02
30.8	0.24	0.22	+0.02	15.5	0.55	0.56	-0.01
32.0	0.22	0.22	0.00	15.3	0.56	0.56	0.00
33.3	0.20	0.22	-0.02	15.0	0.58	0.57	+0.01
33.3	0.20	0.22	-0.02	14.7	0.60	0.58	+0.02
33.7	0.20	0.22	-0.02	15.0	0.58	0.59	-0.01
31.8	0.22	0.23	-0.01	14.7	0.60	0.60	0.00
32.4	0.21	0.23	-0.02	14.8	0.60	0.60	0.00
30.8	0.24	0.24	0.00	14.4	0.63	0.62	+0.01
31.0	0.23	0.24	-0.01	14.3	0.64	0.63	+0.01
31.2	0.23	0.24	-0.01	14.4	0.63	0.64	-0.01
32.0	0.22	0.24	-0.02	14.2	0.65	0.64	+0.01
30.0	0.25	0.25	0.00	14.1	0.66	0.66	0.00
31.1	0.23	0.25	-0.02	14.1	0.66	0.67	-0.01
29.5	0.26	0.26	0.00	14.0	0.67	0.67	0.00
30.4	0.25	0.26	-0.01	13.7	0.70	0.68	+0.02
26.9	0.30	0.27	+0.03	13.8	0.70	0.71	-0.01
28.7	0.27	0.27	0.00	13.9	0.69	0.72	-0.03
29.4	0.26	0.27	-0.01	13.4	0.74	0.73	+0.01
28.4	0.27	0.28	-0.01	13.1	0.77	0.74	+0.03
29.4	0.26	0.28	-0.02	13.3	0.75	0.77	-0.02
27.3	0.29	0.29	0.00	12.9	0.80	0.78	+0.02
27.5	0.29	0.29	0.00	12.3	0.87	0.82	+0.05
25.4	0.32	0.30	+0.02	12.3	0.87	0.90	-0.03
27.1	0.29	0.30	-0.01	11.3	0.96	0.96	0.00
25.3	0.32	0.32	0.00	10.4	1.01	1.01	0.00
25.9	0.31	0.32	-0.01	10.8	0.99	1.05	-0.06
23.5	0.35	0.34	+0.01	9.6	1.07	1.06	+0.01
24.5	0.33	0.34	-0.01				
24.0	0.34	0.35	-0.01				

etc., and it would be necessary to calibrate the instrument for individual conditions.

### SUMMARY

The Carbanalyzer, an instrument for the rapid determination of the carbon content of a steel bath, has been shown in exhaustive tests to be sufficiently accurate to fill a need of the industry. It is relatively inexpensive, requires little upkeep, and can be used by the furnace melter. It may be set up in the open-hearth shop in any reasonably clean location.

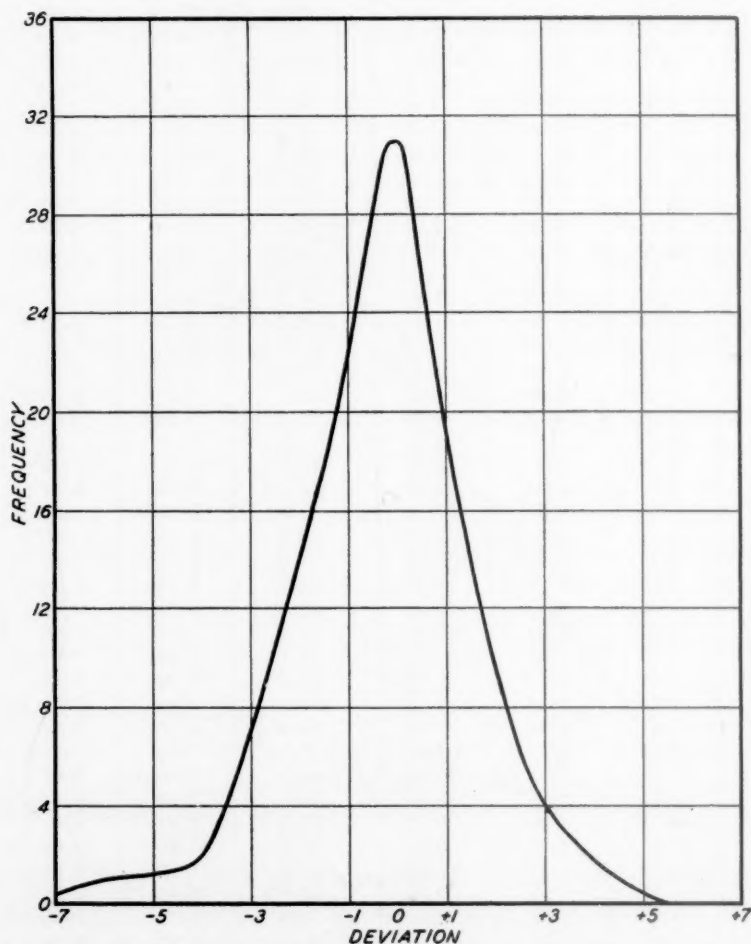


FIG. 7.—FREQUENCY-DEVIATION CURVE FOR THE MILL SAMPLES IN TABLE 1.

Temperature changes cause the current to change slightly, but the instrument is in correct calibration as soon as the current has been set at the correct value. The accuracy of the determination on a single sample has been shown to be good, while the average of three or more samples taken in rapid succession is highly accurate.

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## DISCUSSION

(M. A. Grossmann presiding)

R. C. GOOD,\* Pittsburgh, Pa.—What is the effect of nickel, chrome, copper, manganese, etc., on the readings of this machine? How much aluminum is used to deoxidize the sample taken from the furnace?

H. T. CLARK (author's reply).—The effects of various alloying constituents in the steel sample on the readings of the Carbanalyzer have not been investigated in detail, but it is recognized that some of these affect the results appreciably. In this case, a correction factor, which would depend on the alloy composition of the steel in question, must be applied in order to obtain the correct carbon value.

The amount of aluminum used to deoxidize the sample is not critical, but it must be sufficient to effect a complete deoxidation in order that a sound sample be obtained. The carbon content of the steel and the amount of steel in the spoon will influence this quantity, so that specific values are of significance only when these factors are taken into consideration.

G. MALMBERG,† Surahammar, Sweden.—The Carbanalyzer is like the instrument that I once demonstrated to Aktiebolaget Alpha. I used the same device for adjusting the current and for recording the ballistic deflection. The difference between my first instrument and the Carbanalyzer is that I used the fall of induction from maximum field intensity to zero, whereas the Carbanalyzer uses plus maximum field intensity to minus maximum field intensity. The magnetizations were made by hand. The temperature sensitivity of this apparatus was considerable. A variation of the temperature in the Carbometer, depending on the temperature in the premises,

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led to a change of the resistance of the secondary coil and in the ballistic galvanometer. This influence was so great that the temperature of the Carbometer must be controlled by means of a thermometer and different scales must be used for different temperatures.

Another factor that could not be controlled was the heating of the primary coil by the secondary coil. This disturbance is eliminated in the Carbometer, as the magnetic flux of the permanent magnets does not cause any increase of the temperature. The influence of the temperature in the premises is compensated by means of the special device. The temperature of the Carbometer can therefore be kept comparatively constant. Complete temperature compensation is not possible, for which reason it is advised that the temperature in the premises should be kept as constant as possible.

The influence of the temperature is not avoided in the Carbanalyzer. However, as electric heating of the premises today is available there is no difficulty in keeping the temperature in the works constant, so that the factor of temperature can be eliminated. The other factor, the heating by the primary current, remains. As a weak primary current is used, the heating can be kept comparatively low, but it will still cause some disturbance.

In the Carbanalyzer the same scale is used for both hardened and unhardened specimens. A comparison between readings with the Carbometer and Carbanalyzer gives the following results:

Carbon, Per Cent	Carbometer	Carbanalyzer
0.50	97	16.5
1.00	69	11.0
Difference	28	5.5
0.10	110	38.5
0.30	85	26.5
Difference	25	12.0

The character of the curves in the paper under discussion is the same as that of the Carbometer curves. The frequency curves show deviation of  $\pm 0.03$  per cent for 11 per cent of the values.

In my opinion, the Carbanalyzer is less accurate than the Carbometer.

E. L. RAMSEY,\* South Chicago, Ill.—I understand that this new instrument for the magnetic determination of carbon in a steel bath is similar to the Carbometer and the sampling of the bath is done in a like manner. The speed of the determinations and the portability of the apparatus are very valuable assets. We open-hearth operators always welcome new developments, especially those that give us closer control of the ever-changing steel bath during the process of making a heat. My only criticism is not the instrument described, but the necessity of the accuracy required in taking the samples. It seems that too much depends on the sampling technique, to be absolutely sure that the instrument can give a correct reading. The effect of alloys must also be considered. I believe, however, that better methods of sampling can be developed.

B. A. ROGERS,† Pittsburgh, Pa.—The paper by Work and Clark serves to emphasize the interest in magnetic methods of determining carbon that prevails in the steel

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† Senior Metallurgist, Metallurgical Division, U. S. Bureau of Mines. Discussion published by permission of the Director, U. S. Bureau of Mines.

industry and arises from a number of causes. The rapidity and simplicity of the method and the fact that the apparatus can be used near the furnace encourage the making of frequent analyses, with consequent improvement in control of the furnace. When used for determining the carbon before tapping, the magnetic measurements permit useful furnace time to be saved, and in many instances the amount of ferro-silicon or other substance used in blocking the heat may be reduced materially.

It is probable that several properties could serve as a basis for the development of such a method. The apparatus described by Work and Clark has the merits of portability and simplicity and should be a useful addition to steel-manufacturing equipment.

Has there been any comparison of the analyses of carbon by combustion of samples taken in the mold for the magnetic test and those taken at the same time in the usual box mold? In particular, do both types of samples indicate the same percentage of carbon when the content in the bath is about 1 per cent?

H. K. WORK AND H. T. CLARK (authors' reply).—It is interesting that Mr. Malmberg's early work was with equipment somewhat similar to the Carbanalyzer; his comments indicate that he recognizes certain difficulties that must be overcome before such an instrument will give satisfactory results. In this connection, it is believed that one of the reasons for the successful operation of the Carbanalyzer is the fact that the energy input is kept extremely small. A sensitive meter, a large number of turns in primary and secondary coils, a closed magnetic circuit, and a complete reversal of magnetic flux all contributed to this. No trouble is experienced from heating of the coils by the electric current because the current is only a few milliamperes and thermal equilibrium is quickly established. Changes in ambient temperature are easily compensated for by a simple adjustment in the current, and experiments show that the change in calibration between 50°F. and 86°F. is less than 0.006 per cent carbon, at 0.24 per cent carbon.

In commenting on the accuracy of the Carbanalyzer, Mr. Malmberg undoubtedly has been handicapped by not having an instrument for direct comparison with the Carbometer and his estimation of the relative accuracy of the two instruments is misleading. One division on the Carbanalyzer meter, described in this paper, is equal in size to 3.43 divisions on the Carbometer meter, hence the Carbanalyzer readings must be multiplied by this factor in order to obtain a direct comparison with the Carbometer readings shown. Using this factor, it will be found that the Carbanalyzer scale is somewhat less open in the high-carbon range but considerably more open in the low-carbon range than the Carbometer. The 112 samples in Table 1 were tested on both instruments and the average deviation from combustion values of carbon was found to be slightly in favor of the Carbanalyzer. The over-all accuracy in use of the Carbanalyzer is further enhanced by the fact that but a single setting of the instrument is employed, thus avoiding loss of time and possible error involved in the use of two scales.

In answer to Mr. Ramsey, it is true that it is necessary to exercise care in the preparation of the samples but this does not handicap the operator nor does it prevent him from placing considerable reliance on the results. A series of samples should be taken at frequent intervals during the critical period in the heat and any that are inconsistent may be discarded. It should be a general practice to break each sample after testing in order to detect any obvious pipe or blowholes.

The question of alloy content is more disturbing. If appreciable but unknown amounts of some of the alloying elements are present, no magnetic determinations of carbon are reliable. On the other hand, if the alloy content is known, calibration curves for the type of steel being made can be used with success.

The question raised by Dr. Rogers is a fundamental one in that the success of the magnetic method depends on a consistent agreement between the carbon values as

determined by it and by chemical methods. The Carbanalyzer was calibrated in terms of the carbon content of its own samples determined by the combustion method, and the calibration has been found to be in substantial agreement with the carbon content of corresponding samples taken in the usual box mold. To prevent discrepancies in the two values, it is necessary to avoid the following: (1) decarburization of the hardened magnetic samples during annealing prior to drilling; (2) aluminum content of the magnetic samples greatly in excess of that necessary to kill the steel; and, (3) activity of the steel in the box mold. The first two of these would result in lower carbon values of the magnetic sample while the last would give lower carbon values of the box-mold sample. The primary consideration is a determination of the carbon content of the bath itself and the magnetic sample is made in a manner to give this value as accurately as is possible by a spoon and mold method.

## Tensile Strength and Composition of Hot-rolled Plain Carbon Steels

By C. F. QUEST\* AND T. S. WASHBURN,† MEMBER A.I.M.E.

(New York Meeting, February 1940)

THE steel industry has a definite need in its tonnage mills for a formula relating expected tensile strength to the analysis of the steel. The McWilliam-Barnes<sup>1</sup> and other less comprehensive formulas are used for this purpose, but these formulas were designed for an analysis range that does not include the medium manganese and silicon-bearing steels. This type of steel is being produced to meet the demand for tensile strength slightly higher than that of ordinary structural steel but not high enough to justify expensive alloy steels.

The purpose of this paper is to present a somewhat more comprehensive formula based on data accumulated over a number of years by the Inland Steel Co., and to discuss the method followed in obtaining a formula to fit the data. The resultant formula admittedly is still weak in some respects, but for the expanded analysis range appears to be an improvement over the other formulas. It is hoped that with the collection of more data and possible collaboration with other mills studying this problem it will be possible to work out a more nearly perfect formula.

Several publications have been issued on this subject. In some, the equation type of relation was evolved while others made a combination of tables and an equation. The latter include work by Campbell<sup>2,3</sup> and Webster.<sup>4,5</sup> Campbell classified the steels as acid and basic and applied a different formula to each. For basic steels, he used the equation:

$$\text{Tensile strength} = 41500 + 770C + 1000P + yMn \quad [1]$$

$y$  was a variable depending on the carbon and manganese content of the steel and was listed in tables. Webster investigated acid Bessemer steel and developed the equation:

$$\text{Tensile strength} = 38000 + 800C + xP + yMn \quad [2]$$

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Manuscript received at the office of the Institute Dec. 1, 1939. Issued as T.P. 1182 in METALS TECHNOLOGY, June 1940.

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<sup>1</sup> References are at the end of the paper.



The variables  $x$  and  $y$  depended on the carbon content and were listed in tables.

McWilliam-Barnes and the Bethlehem Steel Co. published the equation type of formula. The McWilliam-Barnes equation was as follows:

$$\begin{aligned} \text{Tensile strength} = & 38000 + C[800 + 4(C - 20)] \\ & + Mn[100 + 2(C - 20)] + 1000P + 120Si \quad [3] \end{aligned}$$

This equation takes into consideration the changing effect of carbon and manganese with variations in the carbon content of the steel. It does not, however, take into account the same change of effect caused by variation in the manganese content. While the original equation contained no allowance for gauge effect, Nead<sup>6</sup> recommended an addition to the calculated value of 1000 lb. for each  $\frac{1}{8}$  in. on sections below  $\frac{3}{4}$  inch.

Arithmetical methods given by the Bethlehem Steel Co.<sup>7</sup> for calculating approximate tensile strength are given in equations 4 and 5.

$$\text{Tensile strength} = 38800 + (650 + 4Mn)C + 90Mn + 1000P \quad [4]$$

$$\text{Tensile strength} = 37430 + 950C + 85Mn + 1050P \quad [5]$$

These equations do not consider either silicon or gauge effect and have limited ranges of application. One of the formulas considers the compounding effect of manganese on the carbon value but the effect of increasing carbon is not expressed. The other formula does not treat this compounding effect at all and is designed for use only in a narrow analysis range where the other formula is not sufficiently in agreement with known physical properties.

In developing a new formula, an attempt was made to establish these complex relations as completely as possible. This was partly successful and by further use of the same method on more complete data, a more comprehensive formula may be obtained.

During recent years data on plain carbon-manganese steel were obtained by the Inland Steel Co. and compiled in graph form as shown in Fig. 1. These curves were used to establish the carbon and manganese expressions in the equation. Test results on silicon-bearing, high-tensile structural steels were used to determine the effect of silicon. These results were all taken from one mill and were within the gauge range of 0.300 to 0.450 inch.

#### MATHEMATICAL METHODS

The data were treated in a manner to determine the individual effect of each element and the variation in this effect caused by change in composition with respect to the other alloying elements. The procedure used was as follows: From Fig. 1, the change in tensile strength on varia-

tion in carbon content at constant manganese ranges,  $\left(\frac{\delta TS}{\delta C}\right)_{Mn}$ , was determined. To evaluate the effect of manganese on this function,  $\left(\frac{\delta TS}{\delta C}\right)_{Mn}$  was plotted against manganese (Fig. 2). The curve was extrapolated to the axis to determine the intercept and the equation of the line determined from the slope and the intercept. This was the general expression\* for the effect of carbon accounting for variations in manganese:

$$\frac{\delta TS}{\delta C} = 700 + 2.94Mn \quad [6]$$

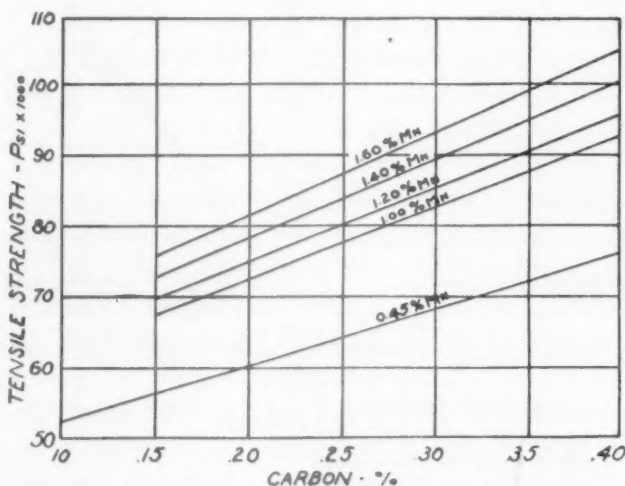


FIG. 1.—EFFECT OF CARBON AND MANGANESE ON TENSILE STRENGTH OF HOT-ROLLED STEEL (0.300–0.450 GAUGE).

To produce a similar expression for manganese, values for  $\left(\frac{\delta TS}{\delta Mn}\right)_C$  were calculated from readings obtained on Fig. 1 as follows:

Tensile strength at 0.25 per cent C and 1.60 per cent Mn = 87100 lb. per sq. in.

Tensile strength at 0.25 per cent C and 1.40 per cent Mn = 83500 lb. per sq. in.

$$\frac{87100 - 83500}{1.60 - 1.40} = \frac{3600}{0.20}, \text{ or } 180 \text{ lb. per sq. in. per point of Mn at } 1.50\% \text{ Mn}$$

Similar calculations were made at several manganese and carbon ranges and the results were plotted on constant carbon lines against the percentage of manganese as the independent variable (Fig. 3). The slopes of these lines representing  $\left(\frac{\delta^2 TS}{\delta Mn^2}\right)_C$  were obtained and plotted against carbon as the independent variable (Fig. 4). This curve permits

\* All symbols for elements in this and other expressions in this article stand for the composition in units of 0.01 per cent; i.e., 0.157 per cent C would be 15.7 in these expressions.

determination of the effect of carbon on the slope of the family of curves in Fig. 3 and establishes a general equation for this slope as follows:

$$\frac{\delta^2 TS}{\delta Mn^2} = 0.48 + 0.0235C \quad [7]$$

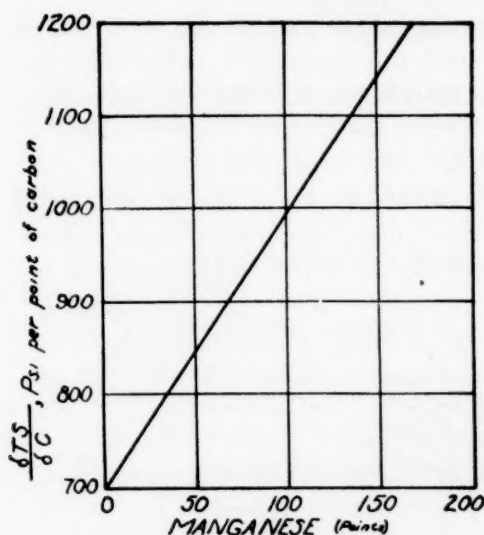


FIG. 2.

FIG. 2.—RELATIONSHIP BETWEEN  $\frac{\delta TS}{\delta C}$  AND MANGANESE CONTENT.

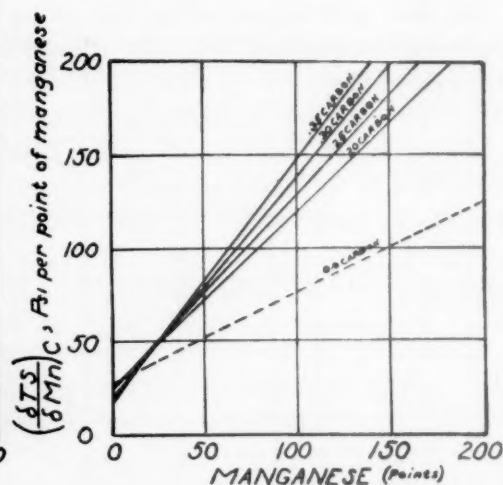


FIG. 3.

FIG. 3.—RELATIONSHIP BETWEEN  $\left(\frac{\delta TS}{\delta Mn}\right)_C$  AND MANGANESE CONTENT.

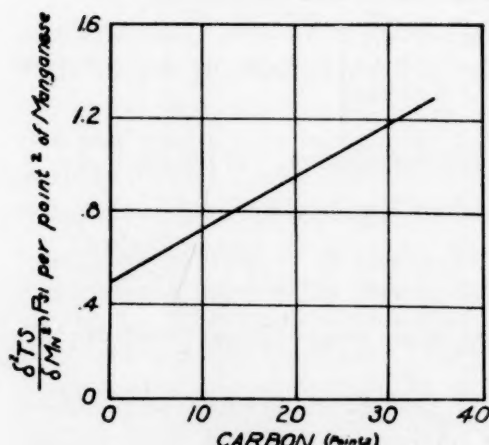


FIG. 4.

FIG. 4.—RELATIONSHIP BETWEEN  $\frac{\delta^2 TS}{\delta Mn^2}$  AND CARBON.

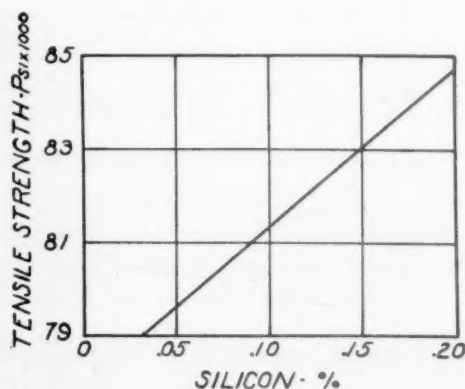


FIG. 5.

FIG. 5.—EFFECT OF SILICON ON TENSILE STRENGTH.

This equation was utilized in locating the hypothetical 0.00 per cent carbon line shown by dashes in Fig. 3. From the intercept of this line and the general expression for the slope of this family of curves, the expression for the general effect of manganese is obtained:

$$\frac{\delta TS}{\delta \text{Mn}} = 30 + \frac{\text{Mn}}{100}(48 + 2.35C) \quad [8]$$

These results were all obtained from data on steels containing no more than 0.05 per cent Si. To determine the effect of silicon, test results on steel in the following analysis ranges were used: carbon, 0.24 to 0.29 per cent; manganese, 1.15 to 1.25; phosphorus, 0.01 to 0.03; silicon, 0.06 to 0.16; gauge, 0.300 to 0.500 in. The test results were classified into one-point ranges of silicon, the averages obtained and graphed as tensile strength versus silicon (Fig. 5). This curve produced the relationship:

$$\frac{\delta TS}{\delta \text{Si}} = 339 \quad [9]$$

These data and other test results indicate that the silicon effect is not described by a straight-line function. However, it was necessary to use that form for silicon in the equation because the data were too limited to evaluate the effect further than the straight-line approximation, or to determine the effect on this function of variations in carbon and manganese. The silicon effect was also checked on steels ranging from 0.65 to 0.75 per cent Mn and a result of the same magnitude was obtained. This silicon value of 340 lb. per sq. in. per point is considerably higher than the McWilliam-Barnes value of 120, but is considered more accurate, especially for silicon ranges above 0.05 per cent.

Further data on silicon steels are being collected to establish the compound effects of carbon and manganese and to confirm the present value.

Since significant variations in phosphorus, with the exception of rephosphorized steels, are relatively uncommon in modern steel practice, the effect of phosphorus was not investigated and the McWilliam-Barnes value of 1000 lb. per sq. in. per unit for this variable will be accepted.

A variation in the gauge of the finished material affects the rate of cooling, as do also the design of the cooling bed and method of disposal, whether cut to sheets and stacked hot, cooled and cut, coiled, etc. These are all in turn dependent on the finishing temperature for the mill under consideration and this is known to vary appreciably. Previous work at the Inland Steel Co. determined this variation as a straight-line function amounting to an increase of 1000 lb. per sq. in. for each decrease in gauge of 0.125 in. This is incorporated into the new equation as  $K$  gauge and is based on material of 0.375 in. according to the following table:

Gauge, in.	$K$ , CORRECTION CONSTANT FOR Gauge, lb. per sq. in.
0.750 and up	-3000
0.625	-2000
0.500	-1000
0.375	0
0.250	+1000
0.125	+2000



Since this gauge effect was determined on material below 1-in. thickness, it is recommended that the gauge correction be limited to material in that range. Very heavy plates, particularly when piled hot, undergo an annealing effect, which may require a large correction, but the conditions governing that effect vary too widely to be covered by a general correction. The data investigated on material below 1 in. led to a correction curve of modified hyperbolic shape, increasing rapidly for light material and approaching a constant value for heavier material. For this reason, it is recommended that a maximum negative correction of -3000 lb. per sq. in. be established, exceptions being made only for the material heavier than 1 in. when test results for a particular case justify it. The gauge correction values given in this paper are a straight-line approximation of the curve mentioned above. This modification was made because individual mill characteristics control this variable to such an extent that any correction more accurate than this would necessarily have to be made for each individual mill, applicable to that mill only.

These individual effects of the several variables were combined into the complete equation, integrating where necessary. The McWilliam-Barnes value of 38,000 lb. per sq. in. for pure iron is a good average result of most work on this subject and will be used in the new equation. A value slightly higher, however, would produce a more favorable comparison between the previous equations 3 and 4 and the new equation 10, particularly in the lower ranges of carbon and manganese. (See discussion in next paragraph and Figs. 6 and 7.) Subject to change by future work, the present form of the new equation is as follows:

$$\begin{aligned} \text{Tensile strength} = & 38000 + C[700 + 2.94 \text{ Mn}] + \\ & \text{Mn}[30 + \frac{\text{Mn}}{200}(48 + 2.35C)] + 340 \text{ Si} + 1000 \text{ P} + K \text{ gauge} \quad [10] \end{aligned}$$

In order to compare the three equations, 3, 4, and 10, two graphs were prepared from calculated results\* on two arbitrary ranges of steel analysis. Fig. 6 is based on an average structural steel with varying carbon, the type of steel for which the McWilliam-Barnes equation was designed. In Fig. 7, the effect of varying manganese at constant carbon for the three equations is shown. In both there is good agreement between the Bethlehem and Inland formulas, and they check fairly well the McWilliam-Barnes formula, although they are slightly lower in the mild structural range. As mentioned previously, this could be corrected by assuming a higher base figure for pure iron than 38,000 lb. per sq. in.

\* Although the McWilliam-Barnes equation 3 originally had no correction for gauge, Nead's recommendation<sup>6</sup> was used to adjust the calculated results for the arbitrary gauge of 0.375 in. The Bethlehem Steel Co. equations 4 and 5 had no gauge correction nor any base gauge figure, so that Nead's correction could not be applied.

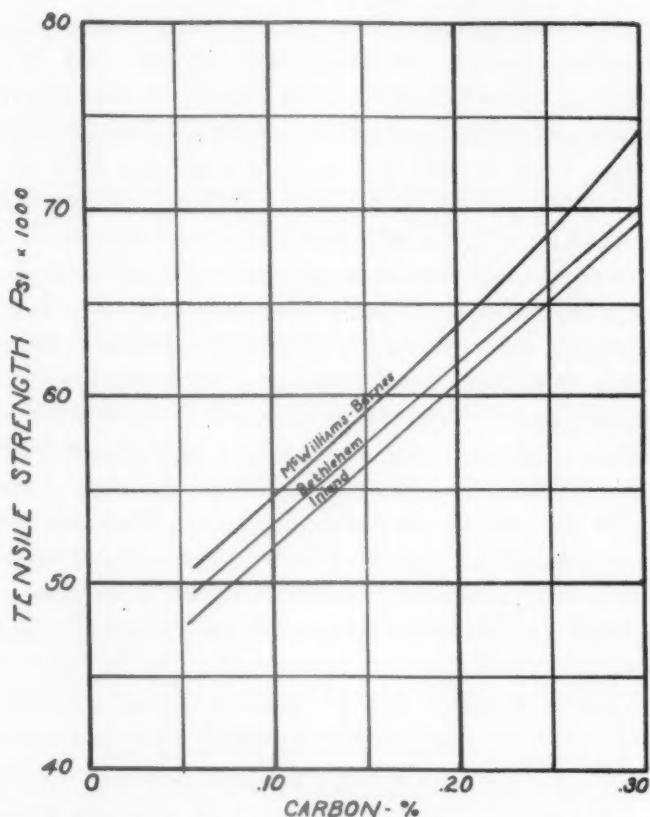


FIG. 6.—TENSILE STRENGTH OF HOT-ROLLED STEEL WITH VARYING CARBON CONTENT AS COMPUTED BY EXISTING FORMULAS.

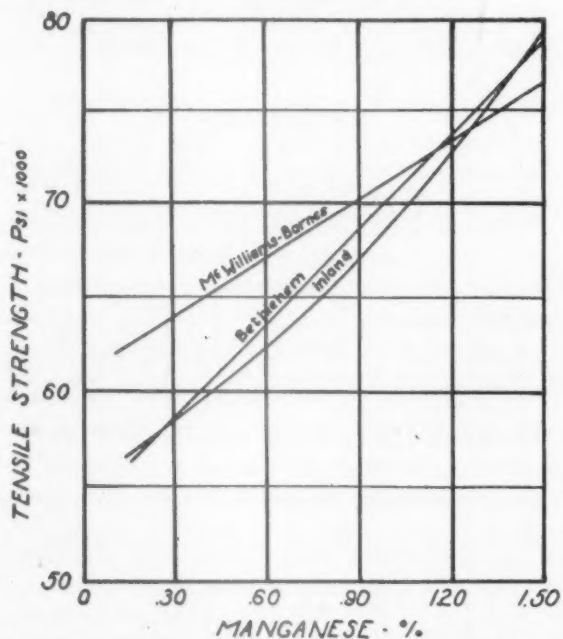


FIG. 7.—TENSILE STRENGTH OF HOT-ROLLED STEEL WITH VARYING MANGANESE CONTENT AS COMPUTED BY EXISTING FORMULAS.

Significant differences appear, however, for high-manganese steels and when appreciable amounts of silicon are present. It is under these conditions that the Inland Steel Co. formula gives superior results.

Equation 10 is considered valid and useful in the following ranges of analysis: carbon, 0.10 to 0.35 per cent; manganese, 0.30 to 1.60; phosphorus, 0.01 to 0.04; silicon, 0.01 to 0.15. Since extrapolation methods were used in treating much of the data, results obtained in the extremes of the chemical range will not be as accurate as those intermediate in the range. More comprehensive data, permitting determination of individual functions as true curves instead of straight-line approximations, will remove this uncertainty and produce a most serviceable equation.

In using this type of formula, it must be considered that the result indicates average expected tensile strength. Results of individual tests may often vary considerably from this calculated value. This deviation may be  $\pm 5000$  lb. per sq. in. where ladle analyses are used. Check analyses on the test pieces usually reduce this by 50 per cent. For this reason it should not be used to check too closely individual cases but rather to predict performance and analysis ranges for specified tensile requirements.

#### ACKNOWLEDGMENT

The authors are indebted to the Inland Steel Co. for the physical test data and statistical summaries on which the calculations of this report are based. They also wish to express their appreciation to Prof. T. L. Joseph, head of the Department of Metallurgy, University of Minnesota, for his assistance in the preparation of this paper.

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## Precipitation-hardening of a Complex Copper Steel

By J. W. HALLEY,\* JUNIOR MEMBER A.I.M.E.

(New York Meeting, February 1940)

COPPER has frequently been recommended as an alloying element for steel and the precipitation-hardening of steels containing from 1 to 2 per cent copper has been studied by a number of investigators.

The straight copper steels, however, have not been used extensively and little advantage has been taken of the precipitation-hardening of complex steels containing appreciable amounts of copper. It is difficult to produce a satisfactory surface on the straight copper steels and undoubtedly this has discouraged their use.

During recent years a number of steels containing enough copper to make them susceptible to precipitation-hardening have been put on the market. These steels belong to the group usually referred to as "low-alloy high-tensile" steels. They were designed for use in the "hot-rolled" condition; transportation equipment and large structures that cannot be readily heat-treated have been their chief application. Little emphasis has been placed on the possibility of strengthening those containing substantial amounts of copper by precipitation-hardening. The present investigation was undertaken to determine the precipitation-hardening characteristic of one of the "low-alloy steels."

### PREVIOUS WORK

The first complete study of the effect of time and temperature on the precipitation-hardening of plain copper steels was made by Nehl<sup>1</sup> in 1930. At about the same time Bucholtz and Koster<sup>2</sup> studied copper-chromium steels but did not determine the relation between time and temperature to produce maximum hardening.

Later, Smith and Palmer<sup>3</sup> determined the rate of hardening at various temperatures for two 1 per cent copper steels containing different amounts of carbon. Their tests indicated that the higher carbon content decreased the rate of hardening. They made tests on many steels containing other alloying elements in addition to copper, but did not determine the time-temperature relationship for maximum hardening for any of the complex steels. Norton,<sup>4</sup> in studying the limit of solid solubility of copper in iron, determined the time for maximum hardening of a 2.06 per cent Cu iron

Manuscript received at the office of the Institute Dec. 11, 1939. Issued as T.P. 1213 in METALS TECHNOLOGY, August 1940.

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<sup>1</sup> References are at the end of the paper.



alloy at three different temperatures. The times did not differ greatly from those found by Smith and Palmer for a 1 per cent Cu steel. Williams and Lorig,<sup>5</sup> in a review of copper steels, give a curve for the relationship between time and temperature for maximum hardening. There

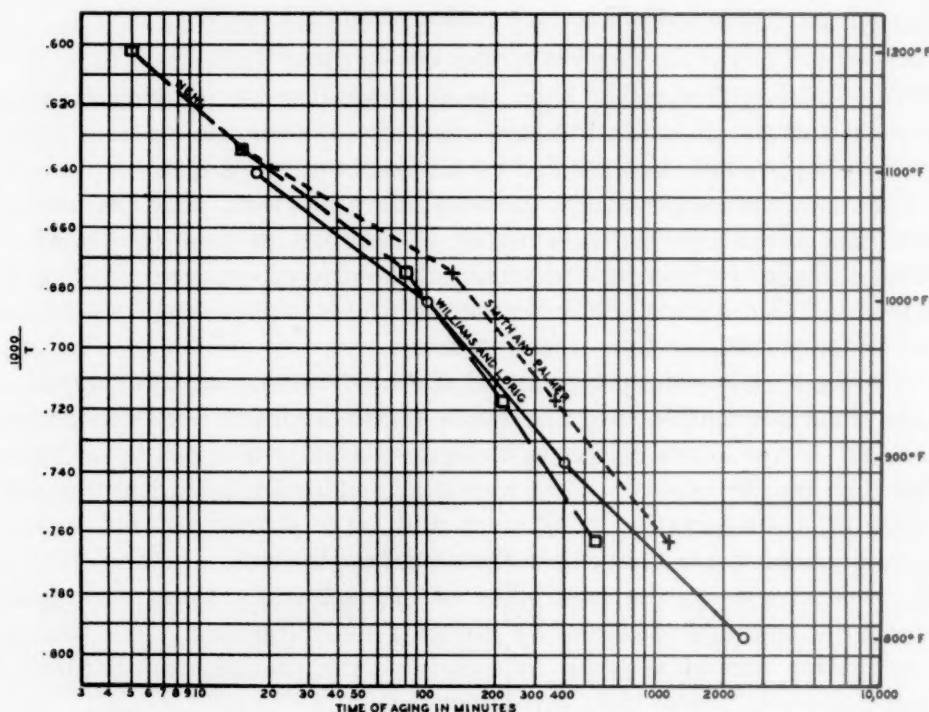


FIG. 1.—TIME TO MAXIMUM STRENGTH OF PLAIN COPPER STEELS.

is a good deal of variation in the time required for maximum hardening as determined by these investigators (Table 1). The differences indi-

TABLE 1.—*Time to Maximum Hardening for 1 Per Cent Copper Steel*

Temperature, Deg. F.	Time to Maximum Hardening			
	Nehl	Smith and Palmer	Norton, 2.06 Per Cent Cu	Williams and Lorig
842	9 hr.	19 hr.		17 hr.
932	3½ hr.	6 hr.	5 hr.	4 hr.
1028	1 hr.	2 hr.		1½ hr.
1112	15 min.	15 min.	5 min.	
1202	5 min.			

cated in the table are probably the result of variations in composition of the steels used by the different investigators, but this cannot be definitely ascertained because only Nehl gives a complete analysis.

For many precipitation-hardening alloys it has been found that a plot of the reciprocal of the absolute temperature against the logarithm of the time to maximum hardness gives a straight line. Such a plot of the available data on 1 per cent plain copper steels is shown in Fig. 1. As a group the data come comparatively close to a straight line. As with other precipitation-hardening alloys, the lower temperatures give the greatest maximum hardness (Table 2). It is advisable to carry out the aging at the lowest practical temperature if maximum strength is desired.

TABLE 2.—*Maximum Increase in Brinell Hardness Obtained at Different Aging Temperatures*

Temperature, Deg. F.	Maximum Increase, Brinell	
	Nehl	Smith and Palmer
842	66	70
932	63	55
1022	58	51
1112	38	55
1202	32	

The results of the aforementioned work on plain copper steels and the scattered data on complex copper steels indicate that a low-alloy steel containing 1 per cent Cu should be susceptible to appreciable strengthening by precipitation-hardening. The variation in results obtained on plain copper steels shows that the rate of hardening must be dependent upon small changes in the steel. Since Norton obtained on a 2.06 per cent Cu steel a rate of hardening similar to the rate for a 1.06 per cent Cu steel found by Smith and Palmer, the rate is not greatly affected by copper content.

#### PRESENT STUDY

A low-alloy steel containing copper, nickel and phosphorus as alloying elements was used in the present study. The aim was to find how the single factor of silicon content affected the rate of precipitation-hardening. Two steels differing primarily in silicon content were used, analyzing as follows: Steel No. 1, 0.09 per cent C; 0.49 Mn; 0.123 P; 0.032 S; 0.188 Si; 0.99 Cu; 0.49 Ni; Steel No. 2, 0.11 C; 0.66 Mn; 0.121 P; 0.025 S; 0.020 Si; 1.16 Cu, 0.57 Ni.

Both steels were deoxidized with aluminum and the only difference in open-hearth practice was that a smaller amount of silicon was added to steel No. 2 than to steel No. 1. Steel No. 1 was in the form of  $\frac{1}{8}$ -in. thick sheet and steel No. 2 in the form of  $\frac{3}{4}$ -in rounds. Both steels were normalized from 1650°F. and tensile-test samples were rough-machined before aging. The normalized properties of the two steels were as follows:

Steel	Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cm. in 2 In.
No. 1.....	56,090	72,890	29.2
No. 2.....	58,750	74,720	34.0

The elongation of the two steels is not comparable because steel No. 1 was tested in sheet form. After aging the samples were finish-machined and pulled. Two tests were made at each time and temperature and the values given are averages of the results. The difference between duplicate tests seldom exceeded 1000 lb. per sq. in. The tensile strength and

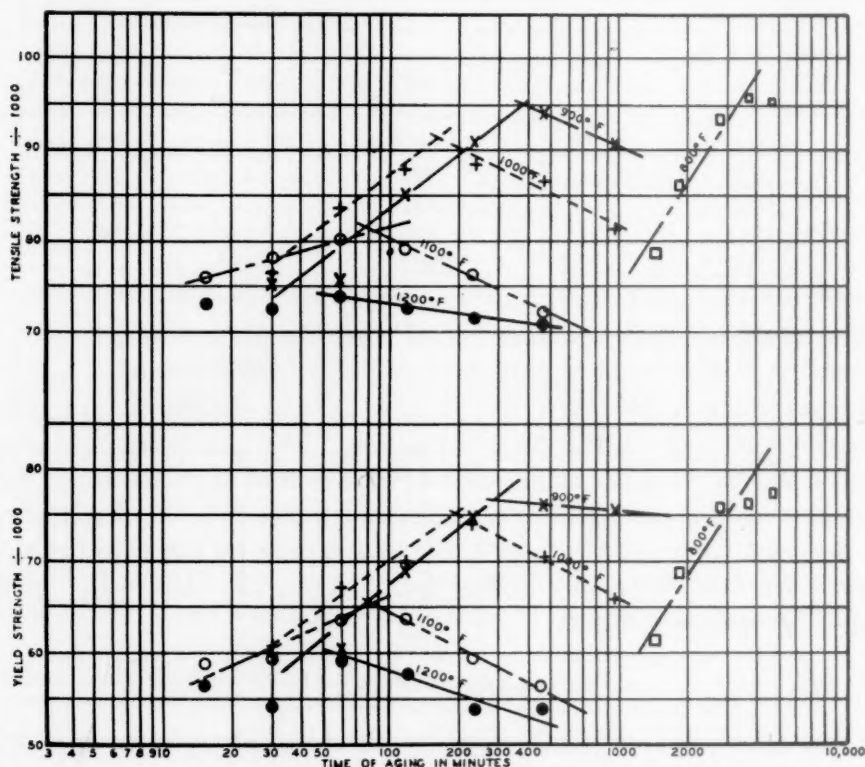


FIG. 2.—AGING OF STEEL NO. 1.

yield strength of steel No. 1 as functions of temperature and time of aging are shown in Fig. 2. Similar curves for steel No. 2 are shown in Fig. 3. Straight lines are arbitrarily drawn through the points because their intersection gives an accurate method for determining the time to maximum strength. In most tests the tensile strength and yield strength reached a maximum at the same time. When there was a discrepancy the tensile strength was used, because it is less susceptible to variations in testing procedure than is the yield strength.

At all temperatures the lower silicon steel, No. 2, required approximately half as much time to reach maximum hardness as did steel No. 1.

The time for maximum strength is given in Table 3 and the logarithm of the time to maximum strength is plotted against the reciprocal of absolute temperature in Fig. 4. The maximum increase in tensile

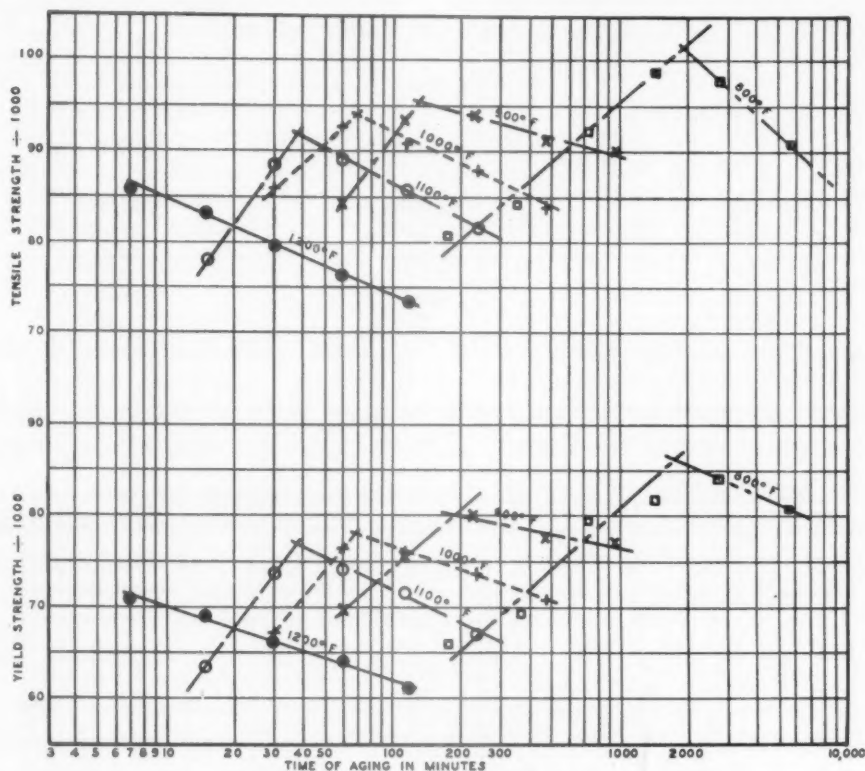


FIG. 3.—AGING OF STEEL NO. 2.

strength obtained at each temperature is shown in Table 4. The increase in strength produced in the higher silicon steel at 1200°F. is negligible.

TABLE 3.—Time to Maximum Strength

Temperature, Deg. F.	Steel No. 1	Steel No. 2
800	70 hr.	32 hr.
900	6 hr. 20 min.	2 hr. 30 min.
1000	2 hr. 30 min.	1 hr.
1100	1 hr. 20 min.	36 min.
1200	40 min.	7 min.

The comparatively short time to maximum strength characteristic of the low-silicon steel recommends it because higher strength may be obtained at lower temperatures, without an impractically long treatment. After precipitation-hardening this steel not only shows an increase in strength that is worth while but retains a remarkable degree of ductil-



ity. Table 5 shows the properties obtained after optimum time at various temperatures.

TABLE 4.—*Maximum Increase in Tensile Strength Produced by Aging at Different Temperatures*

Temperature, Deg. F.	Maximum Increase in Strength, Lb. per Sq. In.	
	Steel No. 1	Steel No. 2
800	22,830	23,930
900	20,830	18,460
1000	15,170	17,380
1100	7,120	14,160
1200	710	11,700

These properties are comparable to those of the lower carbon S.A.E. alloy steels quenched and drawn. The freedom of precipitation-hardened

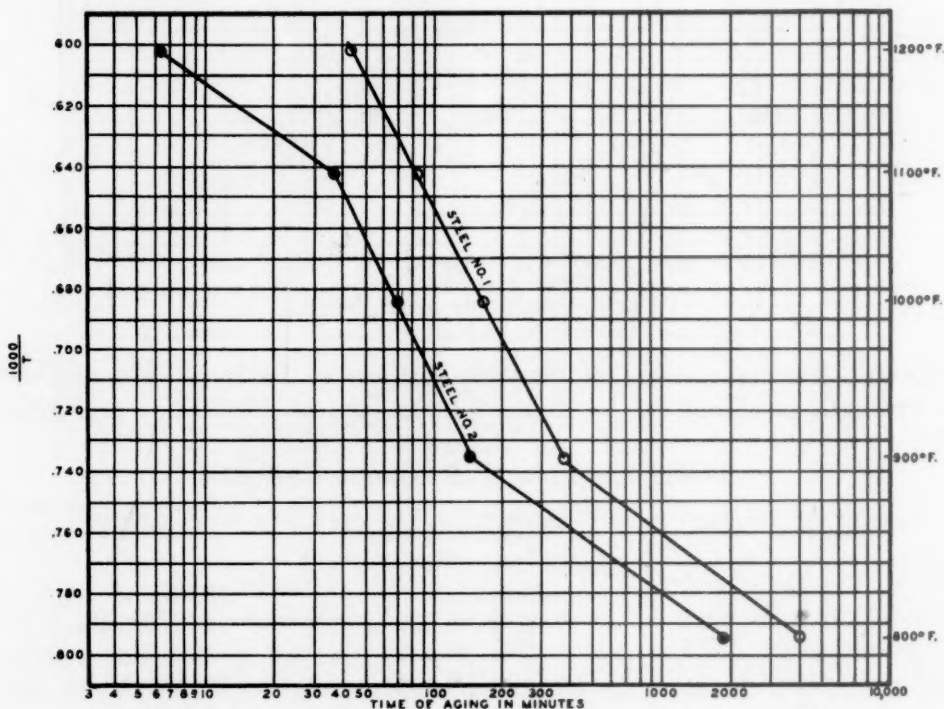


FIG. 4.—TIME TO MAXIMUM STRENGTH OF COMPLEX COPPER STEELS.

steels from distortion and mass effect is a decided advantage whenever extremely high strength is not required. An interesting possibility of this steel is that it may be cold-formed in the most ductile, normalized or hot-rolled condition, followed by precipitation-hardening to maximum strength.

TABLE 5.—*Physical Properties Obtained by Precipitation-hardening of Low-silicon Copper-nickel-phosphorus Steel*

Temperature, Deg. F.	Time of Treatment	Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent	Reduction of Area, Per Cent	Rockwell Hardness, B
800	32 hr.	81,470	98,650	27.0	62.2	93
900	2 hr. 30 min.	80,200	93,800	26.0	64.0	90.5
1000	1 hr.	76,640	92,100	27.8	65.8	89
1100	36 min.	74,300	88,900	27.0	65.6	88
1200	7 min.	71,730	86,420	28.0	67.4	86.5

## SUMMARY

In this study it was found that silicon had a marked effect on the precipitation-hardening rate of a copper-nickel-phosphorus steel. By reducing the silicon content from 0.188 to 0.020 per cent the precipitation-hardening rate was more than doubled.

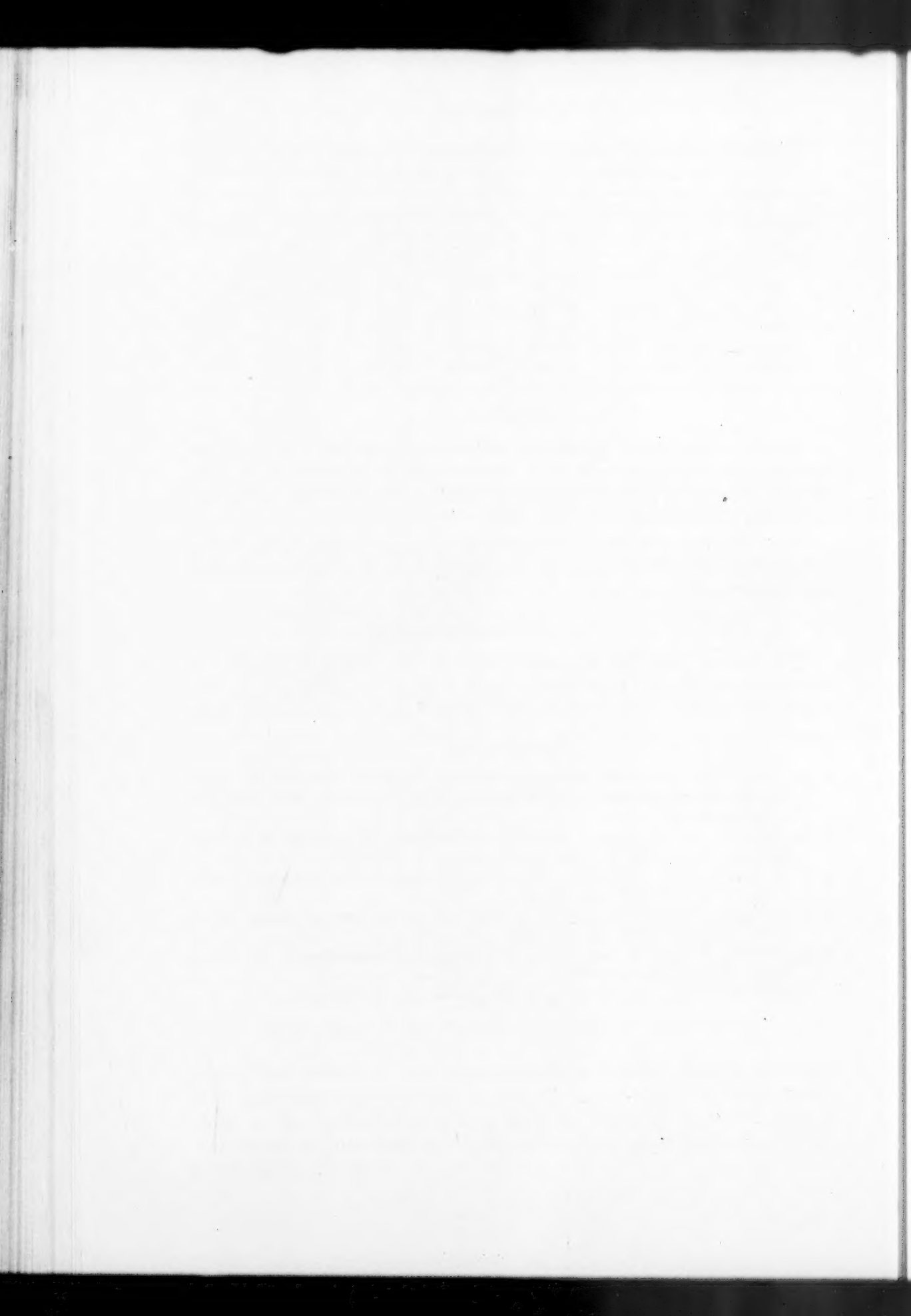
The physical properties resulting from a precipitation-hardening treatment of the low-silicon steel were equal to those of many quenched and drawn steels.

## ACKNOWLEDGMENTS

The author expresses his appreciation to the Inland Steel Co. for permission to use the experimental data and results submitted in this paper, and to Mr. J. H. Nead for his helpful suggestions and criticisms.

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